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VOLUME XXIX

• NUMBER FOUR

RUBBER CHEMISTRY

AND TECHNOLOGY

PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY





KOSMOS 60

Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil, and its manufacture is scientifically controlled to meet the highest standards. Its superb processing and balance of strength make for the best in rubber products.

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New York • Akron • Chicago • Boston • Memphis
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PHILBLACK* makes rubber do tricks for you!

Your rubber compound "performs" better with the proper Philblack. For example, using Philblack A helps remove nerve, speeds up processing, and improves both the molding and extruding qualities of rubber.

And in the finished product the Philblacks are star performers! It is no trick for Philblack E to add much more wear to cold rubber tire treads.

And Philblack I plays a double role. It maintains a good balance between abrasion resistance and costs . . . producing sturdy tires in the moderate price range.

To find out which Philblack will perform best for you, consult your Philblack technical representative. Get complete information about the Philblacks, the family of high quality carbon blacks with an international reputation for good performance!

*A trademark



Meet the Philblacks!

DISCOVER WHAT THEY'LL DO FOR YOU!



Philblack A FEF Fast Extrusion Furnace Black

Ideal for smooth tubing, accurate molding, satiny finish. Mixes easily. High, hot tensile. Disperses heat. Non-staining.



Philblack I ISAF Intermediate Super Abrasion Furnace Black

Superior abrasion resistance at moderate cost. Very high resistance to cuts and cracks. More tread miles at high speeds.



Philblack O HAF High Abrasion Furnace Black

For long, durable life. Good electrical conductivity. Excellent flex. Fine dispersion.



Philblack E SAF Super Abrasion Furnace Black

Toughest black on the market. Extreme abrasion resistance. Withstands aging, cracking, cutting and chipping.



PHILLIPS CHEMICAL COMPANY, Rubber Chemicals Division, 318 Water St., Akron 8, Ohio

Export Sales: 80 Broadway, New York 5, N. Y.

West Coast: Harwick Standard Chemical Company, Los Angeles, California.

Entered as second-class matter March 19, 1943, at the Post Office at Lancaster, Pa., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in paragraph (d-2), Section 3440, P. L. and E. of 1948, authorized September 25, 1940.

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... count on witco-continental!

Rigid quality control is a key factor in Witco-Continental's 5 modern carbon black manufacturing plants. Our job is to produce uniform products to meet your requirements.

Witco-Continental has developed its manufacturing and technical service facilities to serve the rubber industry better. Our advice and assistance are at your disposal. For help with your rubber black problems, call your nearest Witco office.

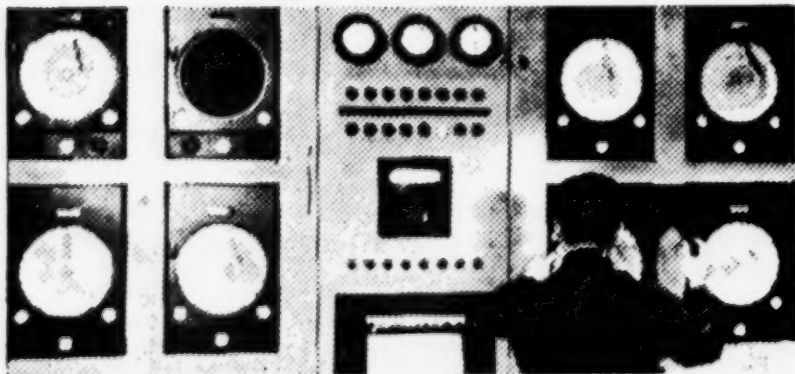


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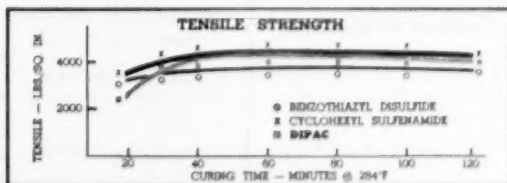
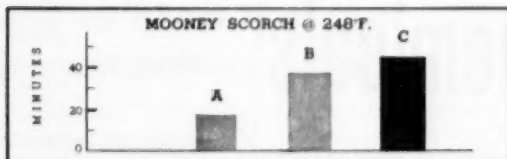
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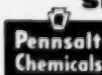
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Akroflex C	Akroflex CD	Neozone D
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Aquarex G	Aquarex NS
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Rubber Red 2BD	Rubber Blue PCD
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Rubber Green FD	Rubber Orange OD

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Barak —Accelerator activator	Ing agent
Copper inhibitor x-872-L —Inhibits catalytic action of copper on elastomers	HELIOZONE —Sun-check-Ing inhibitor
ELA —Elastomer lubricant	NBC —Inhibits weather cracking of GR-5
	RETARDER W —Accelerator retarder

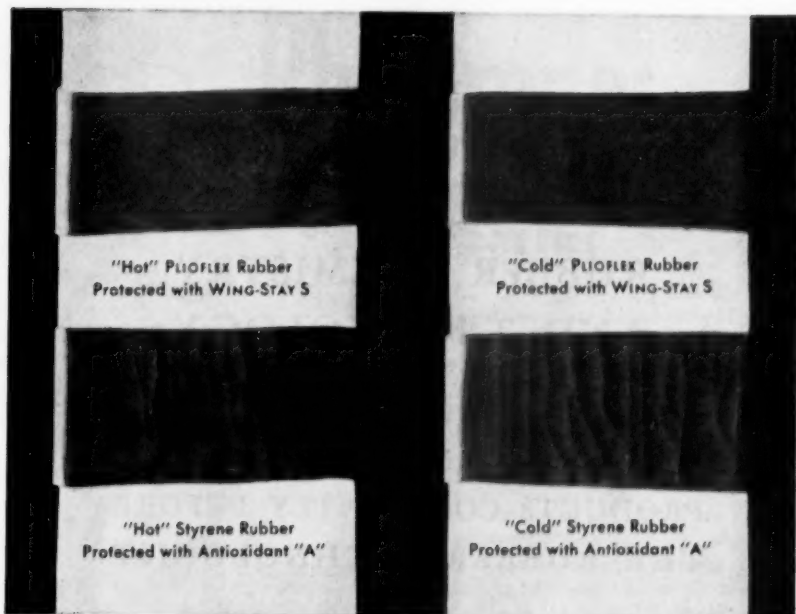
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In Canada contact: Du Pont Company of Canada Limited,
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NOTE: All samples exposed to direct sunlight for three weeks

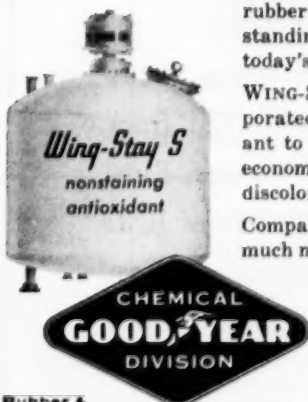
How to stop the sun In its attack on rubber

Exposure to sunlight can result in premature surface hardening and cracking of both natural and synthetic rubber goods. But *not* if you use WING-STAY S—the outstanding, nonstaining, non-discoloring antioxidant on today's market.

WING-STAY S is a liquid styrenated phenol. Easily incorporated into dry rubber or latices, it is extremely resistant to heat, sunlight or extraction by water—provides economical protection against aging with a minimum of discoloration, odor or migration.

Compare the test pieces pictured above. They show how much more protection WING-STAY S gives styrene rubber against direct sunlight than does another well-known nonstaining antioxidant. Your own tests will give you further proof of its superiority. So write, today, for samples and the latest *Tech Book Bulletins*. The address:

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High Polymer Resins, Rubbers, Latices and Related Chemicals for the Process Industries

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KEEP YOUR NAME AND YOUR
PRODUCTS CONSTANTLY BEFORE
THE RUBBER TECHNOLOGIST

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Philprene*

**brings you rubber
à la carte!**


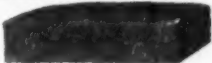
Coming up . . . and just the way you like it! You can order from a menu consisting of 17 different Philprene polymers and masterbatches. By selecting the proper Philprene, you get the particular characteristics you need in your operation.

Tell us what qualities you require . . . physical properties . . . compound cost . . . rapidity of mixing . . . extrusion rate . . . die swell or shrinkage . . . staining, etc. Then let our technical representative suggest the proper Philprene to use to get optimum results.

We are glad to help you with all kinds of technical problems . . . to assist you in the efficient and profitable use of Philprene.

*A trademark

CURRENT PHILPRENE RUBBERS

	POLYMERS 	PHILBLACK® MASTERBATCHES 
HOT	PHILPRENE 1000 PHILPRENE 1009 PHILPRENE 1001 PHILPRENE 1018 PHILPRENE 1006 PHILPRENE 1019	
COLD	PHILPRENE 1500 PHILPRENE 1502 PHILPRENE 1503	PHILPRENE 1601 PHILPRENE 1605
COLD OIL	PHILPRENE 1703 PHILPRENE 1706 PHILPRENE 1708 PHILPRENE 1712	PHILPRENE 1803 PHILPRENE 1806—similar to Philprene 1803 but incorporating 50 parts of PHILBLACK I.

PHILLIPS CHEMICAL COMPANY

Rubber Chemicals Division • 318 Water Street, Akron 8, Ohio



...headed for a fall

Your profits are headed for a fall unless you take advantage of ways to lower your material cost without decreasing quality. Numerous tests and actual performance have proved that with the use of **TEXAS "E" and TEXAS "M" CHANNEL BLACKS**, alone or in blends with other blacks, worthwhile savings can be made with no loss in ultimate performance.

Our customers' needs, present and future, are assured by our own nearby, natural resources and the world's largest channel black plant.



Sid Richardson
C A R B O N C O.

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Looking for a cost cutting,
quality building
miracle additive?

USE VELSICOL

hydrocarbon resins
to make better rubber
products, build
quality and cut costs!



Here are the facts!

PHYSICAL PROPERTIES	GE-9	AB-11-4	X-30
Type	Thermoplastic Hydrocarbon Solid or Powder	Thermoplastic Hydrocarbon Solid or Flaked	Thermoplastic Hydrocarbon Solid or Flaked
Form			
Specific Gravity @ 60°F	1.13-1.15	1.09-1.02	—
Weight per gallon @ 60°F (lbs.)	9.41-9.58	9.08-9.33	—
Bulking Value @ 60°F	0.1044-0.1052	0.1074-0.1102	—
Softening Point (Ball and Ring)	220°-230°F	220°-230°F	210°-220°F
Color (Coal Tar Scale)	20-22	3½-4½	1½-2*
Acid No.	0-2	0-2	0-2
Saponification No.	0-2	0-2	0-2

*Color: Gardner: 10-11; Rosin Scale: I-K.

These resins also have exceptionally good electrical insulation properties, because they are hydrocarbon polymers. Compatible with a variety of natural and synthetic rubber compounds.

FOR: battery cases, electrical insulation, rubber shoe soles and heels, rubber floor tiling, gaskets and jar rings, hard rubber compounds, tubular compounds, mechanical goods, rubber adhesives and cements, reclaimed rubber, molded rubber products, colored rubber stocks.

ADVANTAGES: better milling, calendaring, and tubing; more uniform cures, non-scorchy stocks; greater toughness, hardness, resistance to tearing, aging and abrasion; improved tensile strength and elongation; lower raw materials costs.

Write for
Technical Bulletin 218.

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CHEMICAL CORPORATION

Dept. 99 330 East Grand Ave., Chicago 11, Illinois



RUBBER COMPOUNDERS: Do you know you can

SAVE
\$ 1200⁰⁰
 up to **per carload**
on resin costs
 with **PANAREZ**
HYDROCARBON RESINS!

If you compound rubber, *low cost* PANAREZ hydrocarbon resins offer definite advantages. These softeners are available in any color from Barrett No. 1 to 18, and softening point from 40°F. to 300°F. They are supplied in flaked or solid form. Immediate delivery.

Compounds containing PANAREZ RESINS
 show these characteristics:

- Improved color and color stability
- Improved extrudability
- Improved flex-crack performance
- Improved abrasion resistance
- Improved ozone resistance
- Improved tear resistance
- Improved tensile strength and elongation

No change in compounding technique is required when switching to Panarez resins.

For samples and detailed information, write us, telling the intended application.

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 CORP *Chemicals*

555 FIFTH AVENUE, NEW YORK 17, N. Y.



PANAPOL
 Hydrocarbon drying oils

PANASOL
 Aromatic solvents



Making Customers Feel Like This Is Our Business

Something new every day in the rubber business. But juggling your formulations with new materials doesn't have to make you feel glum. Monsanto's Rubber Service Department at Akron keeps tab on *every new material* that comes out; is ready to assist you with up-to-the-minute data to guide your formulations. Take the job of producing a good heat-resistant butyl insulation stock:

The Problem: Produce a high-voltage butyl insulation stock.

Here's What Monsanto Compounders Did: Compounded stock of Enjay Butyl 218 (GRI-18) containing one part of Sulfaslan R and compared it with standard butyl formulations.

The Result: The Sulfaslan R stock after aging 48 hours at 300° F. showed the best retention of tensile strength, elongation, and hardness.

Helping you get the results you want is the only way we can sell. You're not interested in chemicals; but you are interested in *performance* at lowest possible cost. That's why manufacturers of rubber products

discuss their processing and end-product requirements with Monsanto. Often, no special research is even needed—the answer to your formulating problem may already be on file among the more than 18,000 special research reports covering studies that Monsanto Akron has carried out for rubber processors. Write or call: *Monsanto Chemical Co., Rubber Chemicals Dept. RC-3* (telephone: HEmlack 4-1921), Akron 11, Ohio.

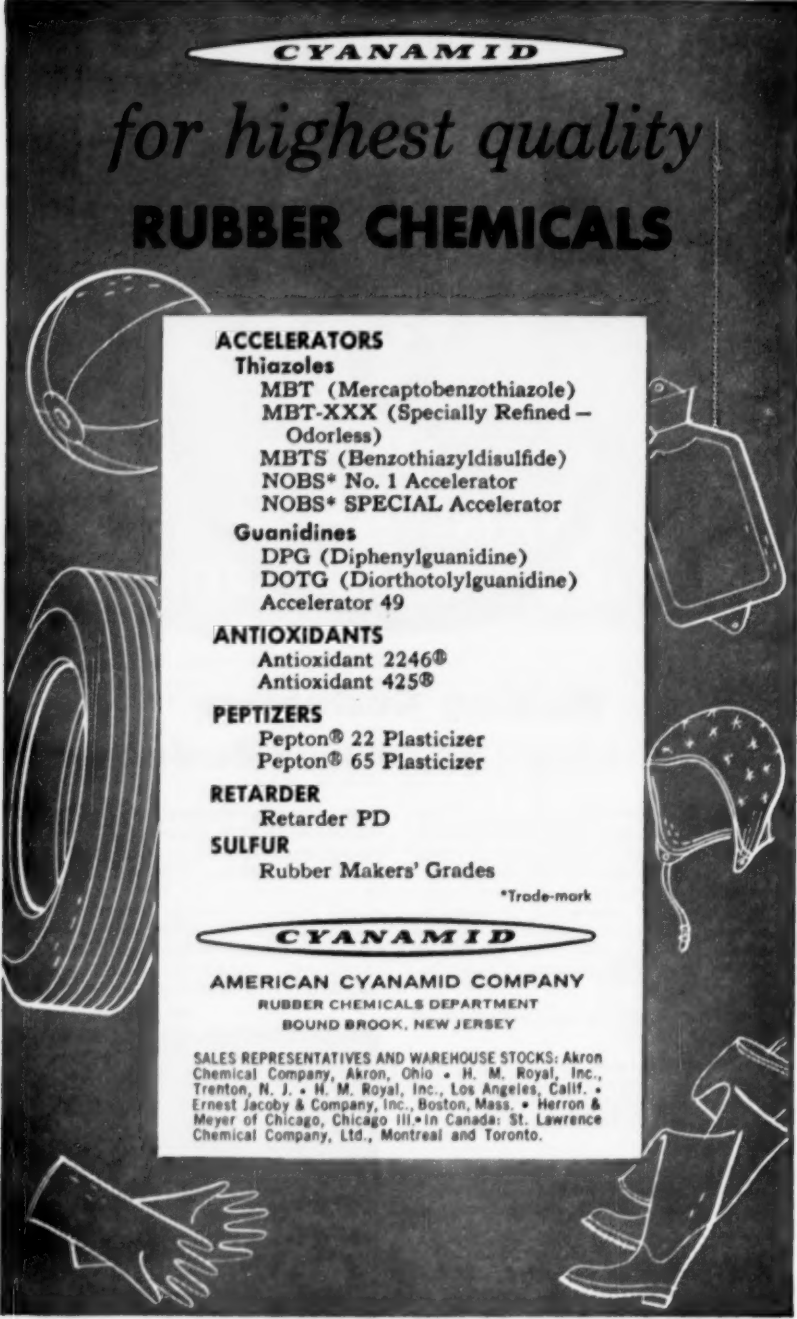
SULFASLAN, Reg. U. S. Pat. Off.

Accelerators • For fast, slow, and regulated rates of safe cure.

Antioxidants • For maximum oxidation resistance.

Specialty Compounds • For special processing problems.



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for highest quality
RUBBER CHEMICALS

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- NOBS* No. 1 Accelerator
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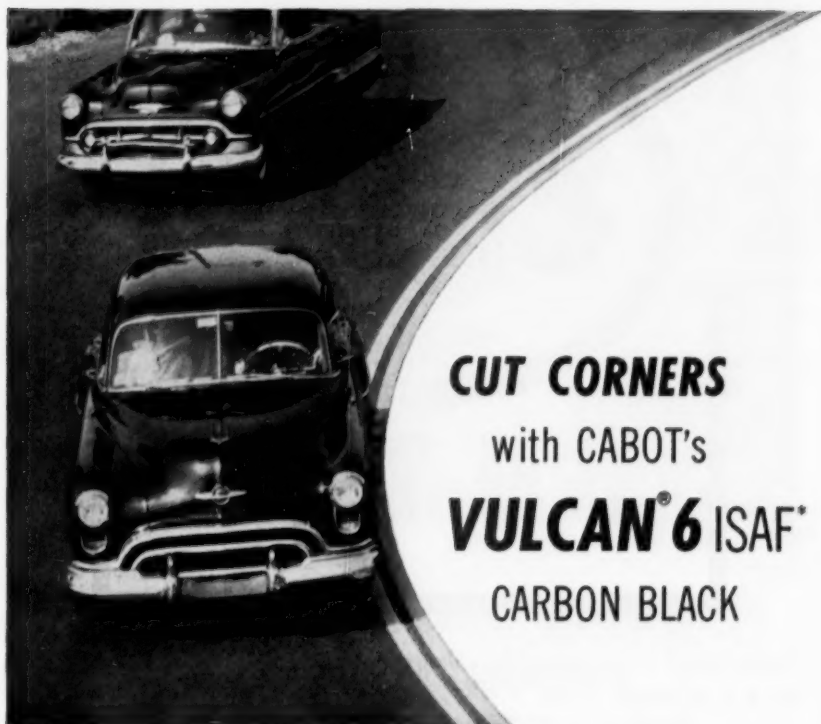
- Rubber Makers' Grades

*Trade-mark

CYANAMID**AMERICAN CYANAMID COMPANY**

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CUT CORNERS
with CABOT's
VULCAN® 6 ISAF*
CARBON BLACK

For NO-SQUEAL, LONGER WEARING TIRES,
specify VULCAN 6. Minimize tire squeal and at the same
time improve the wear of low hardness treads.

Vulcan 6 provides a single answer to both problems.
Try Vulcan 6 . . . the CABOT high quality ISAF
standard of the carbon black industry.

CHANNEL BLACKS: Spheron 9 EPC • Spheron 6 MPC • Spheron C CC
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Vulcan C CF • Sterling 99 FF • Sterling SO PEF • Sterling V GPF • Sterling L HMF
Sterling LL HMF • Sterling S SRF • Pelletex SRF • Pelletex NS SRF
Sterling NS SRF • Sterling R SRF • Gastex SRF
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**Intermediate Super Abrasion Furnace*

Free Samples, Technical Literature Available



GODFREY L. CABOT, INC.

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Enjay Butyl is the super-durable rubber with outstanding resistance to aging • abrasion • tear • chipping • cracking • ozone and corona • chemicals • gases • heat • cold • sunlight • moisture

Know the facts about fabulous BUTYL

Here are some of the reasons for the rapidly increasing acceptance of Enjay Butyl for more and more rubber applications in more and more industries.

- Molded mechanical goods like body bumpers and auxiliary springs, outperform those made of natural rubber or GR-S types.
- Good hot tear resistance reduces percentage of mold removal rejects, thus reduces costs.
- Excellent adhesion is obtained to fabrics and metals.
- Thermal interaction of Butyl with carbon black improves properties such as abrasion and resilience.
- Non-staining grades of Enjay Butyl do

not fade or discolor on exposure to light or weather.

- Moldings and extrusions do not crack from sunlight or weather exposure and they retain new appearance and performance longer.
- Has excellent electrical properties plus resistance to ozone, corona, moisture absorption and abrasion, that is outstanding.
- Resists both heat and aging in high voltage insulation compounds.
- Low cost . . . immediate availability.

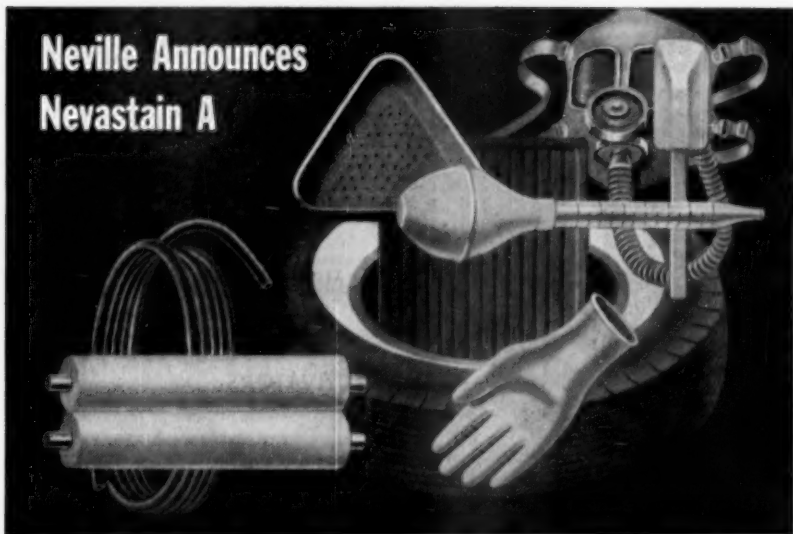
Get *all* the facts by writing or calling the Enjay Company. Complete laboratory and testing facilities are at your service.



Pioneer in Petrochemicals

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A New Non-Staining Rubber Antioxidant with Superior Characteristics

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NEVILLE

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Naugatuck Chemical



Division of United States Rubber Company
Naugatuck, Connecticut

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INSULATION**

Current NAUGAPOL Polymers for electrical applications

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GRADE	CLASS	END USES
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GRADE	CLASS	END USES
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NAUGAPOL 1504	Non-staining	Low styrene content. Wire and cable and mechanical goods for arctic service.

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Naugatuck Chemical

Division of United States Rubber Company
Naugatuck, Connecticut



IN CANADA: NAUGATUCK CHEMICALS, Elmira, Ontario • Cable Address: Rubexport, N. Y.
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OIL EXTENDED POLYMERS GR-S TYPES 1705 1709 1710	SUNDEX-53	Versatile. Highly compatible with natural rubber, reclaims, GR-S types.
NEOPRENE WHV	SUNDEX-53	Cost of compounds comparable to low-cost elastomers.
REGULAR NEOPRENES and NATURAL RUBBER	CIRCO LIGHT RUBBER PROCESS-AID	True softening by physical changes in rubber structure. Large quantities absorbed without blooming.

To learn more about using Sun Rubber Process Aids to get better physicals, lower costs, and easier processing, see your Sun representative. Or write for your copy of Sun's latest Technical Bulletin describing any of the above products. Address: SUN OIL COMPANY, Philadelphia 3, Pa., Dept. RC-10.

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PHILADELPHIA 3, PA.

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PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY



COLUMBIAN CARBON BLACKS

for RUBBER COMPOUNDING

STATEX-125 ISAF (Intermediate Super Abrasion Furnace)

STATEX-R HAF (High Abrasion Furnace)

STANDARD MICRONEX® MPC
(Medium Processing Channel)

MICRONEX W-6 EPC (Easy Processing Channel)

STATEX-B FF (Fine Furnace)

STATEX-M FEF (Fast Extruding Furnace)

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RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor, representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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 Terms end October 1956. Meetings in 1956: February 15, March 21, April 18, May 16.

FUTURE MEETINGS

Meeting	City	Hotel	Date
1956 Spring	Cleveland	Cleveland	May 16-18
1956 Fall	Atlantic City	Chalfonte-Haddon Hall	September 19-21
1957 Spring*	Montreal	Sheraton-Mt. Royal	May 15-17
1957 Fall	New York	Commodore	September 11-13
1958 Spring	Cincinnati	Netherlands Plaza	May 14-16
1958 Fall	Chicago	Sherman	September 10-12
1959 Spring	Buffalo	Statler	May 13-15
1959 Fall	Atlantic City	**	September 16-18

* Joins meeting with the Rubber Division of the Canadian Institute of Chemistry.

** Hotel not yet assigned by the American Chemical Society.

CHARLES GOODYEAR MEDAL AWARD FOR 1957

To all members of the Division of Rubber Chemistry:

This letter is for the purpose of soliciting proposals for candidates for the Charles Goodyear Medal Award for consideration by the Medal Committee at the Spring meeting to be held in Montreal, May 15-17, 1957.

Your proposals should be presented in the form suggested in the *Outline for Proposal* given below, and mailed to the Division Secretary, Dr. Neal, so as to reach him not later than April 12.

For your guidance, I am listing below the past Goodyear Medalists and also a list of fields not yet fully recognized. Additional awards in fields already recognized, e.g., polymerization and vulcanization, are, of course, in order. The by-laws do not prohibit the election of a foreign technologist.

I hope that each of you will consider this matter carefully.

A. E. Juve, Chairman
Charles Goodyear Medal Committee

OUTLINE FOR PROPOSAL OF A CANDIDATE

FOR THE

CHARLES GOODYEAR MEDAL AWARD

1. Name of candidate.....
2. Statement of contribution of candidate for use for the Award Citation.....

3. General statement concerning the importance of such contribution.....
4. Pertinent publications of the candidate.....
5. Brief biography of the candidate.....
6. Name, address, and signature of proposer member of the Division of Rubber Chemistry.....

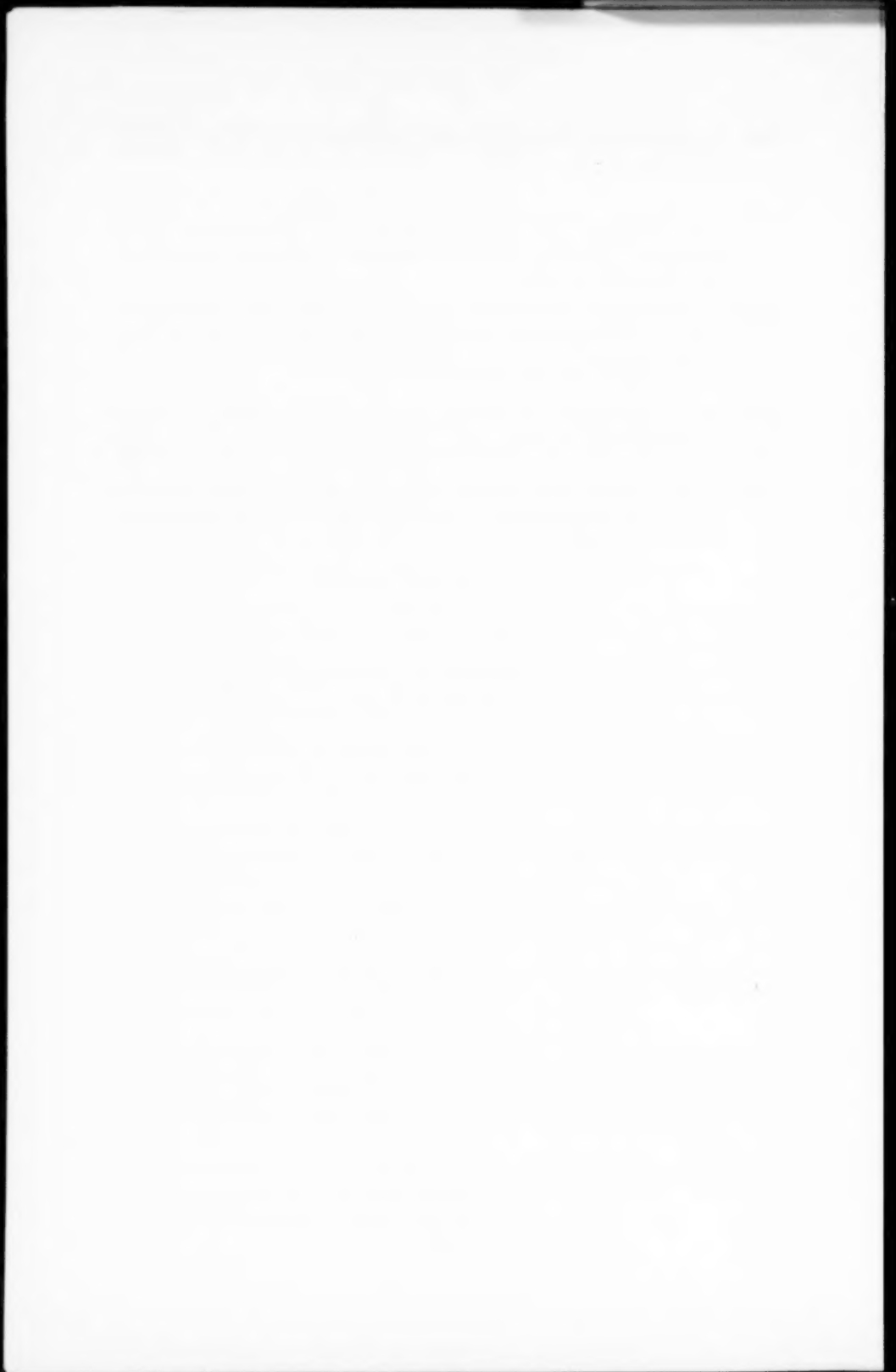
FIELDS NOT YET FULLY RECOGNIZED

Among fields which have not been fully recognized may be mentioned: Physics of rubber, including kinetic theory, dynamic and electrical properties; reinforcement; oxidation; antioxidants; polysulfide rubbers (Thiokol); polychloroprene (Neoprene); vulcanizable copolymers of isobutylene and dienes (Butyl); cold GR-S and oil-extended GR-S; polyacrylate rubbers; silicone rubbers; isocyanate rubbers; reclaiming; physical testing; delayed-action accelerators; new reinforcing fillers; new processing equipment.

CHARLES GOODYEAR MEDALISTS

- 1941 DAVID SPENCE. A pioneer of rubber chemistry, who did much important early work. No lecture given.
- 1942 L. B. SEBRELL. Research on antioxidants and accelerators. Lecture: "The Second Mile", *Industrial and Engineering Chemistry*, 1943, p. 736; *RUBBER CHEMISTRY AND TECHNOLOGY*, 1943, p. 713.
- 1944 W. L. SEMON. Synthetic rubber research. Lecture: "Research leading to commercial butadiene synthetic rubber", *Chemical and Engineering News*, 1946, p. 2900; *India Rubber World*, December 1946.
- 1946 IRA WILLIAMS. Neoprene and overall accomplishments. Lecture: "Vulcanization of rubber with sulfur", *Industrial and Engineering Chemistry*, 1947, p. 901.
- 1948 GEORGE OENSLAGER. Pioneer in organic accelerators. No lecture given.
- 1949 H. L. FISHER. Long in the field of rubber chemistry; over all accomplishments. Lecture: "Rubber research and the need for a rubber research institute in the United States".
- 1950 C. C. DAVIS. Development of the oxygen bomb test for accelerated aging; *Chemical Abstracts*; *RUBBER CHEMISTRY AND TECHNOLOGY*; Editor "The Chemistry and Technology of Rubber". Lecture: "Some of the real pioneers of the rubber industry", *India Rubber World*, 1951, p. 433.
- 1951 W. C. GEER. Oven aging test, de-icer for airplanes, encouragement of rubber research. Lecture: "Strategy in rubber research". *Industrial and Engineering Chemistry*, 1951, p. 2436.

- 1952 H. E. SIMMONS. One of the early and best known teachers of rubber chemistry, and an inspirational guidance of younger men. Lecture: "Out of the past".
- 1953 J. T. BLAKE. Research on oxidation and vulcanization. Co-editor of "The Chemistry and Technology of Rubber". Accumulative accomplishments. Lecture: "The future of rubber". *Chemical and Engineering News*, 1953, p. 4290.
- 1954 G. S. WHITBY. Research on plantation rubber, vulcanization, accelerators, GR-S synthesis, overall accomplishments. Editor of "Synthetic Rubbers". Lecture "Reflections on rubber research". *Industrial and Engineering Chemistry*, 1955, p. 806.
- 1955 R. P. DINSMORE. Numerous important contributions to rubber chemistry and technology; recipient of honors. Lecture: "Specifications for a rubber chemist". *Rubber World*, Vol. 134, No. 1, p. 57, April 1956.
- 1956 S. M. CADWELL. Contributions to the field of rubber chemicals and to the control of vulcanization. Lecture: "Scientific Contributions to the Rubber Industry".



THE POLYMERIZATION OF VINYL MONOMERS IN NATURAL-RUBBER LATEX *

GEORGE F. BLOOMFIELD AND P. McL. SWIFT

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
WELWYN GARDEN CITY, HERTFORDSHIRE, ENGLAND

INTRODUCTION

Polymerizations of various vinyl monomers dispersed in natural rubber latex have been described in the literature¹. These involve either the admixture of monomer with a stabilized latex or the addition of an emulsified monomer to latex, followed by the introduction of an initiator which brings about the polymerization of a major proportion of the added monomer under convenient conditions of time and temperature. Refinements in the technique consist of deammoniating the latex when using systems which are sensitive to free ammonia or to ammonium ions, adjustment of pH to suit specific initiators, flushing with an inert gas in systems sensitive to inhibition by oxygen, and using a mutual solvent with monomers which are not very soluble in rubber.

Recently it has been shown that when certain organic peroxides are used to initiate polymerization of monomers in the presence of rubber, the latter is extensively modified by combination with polymer². In order to achieve this desirable state of affairs in a practical latex system, it is necessary that the monomer is absorbed by the rubber particles and that polymerization takes place within the swollen globules. Otherwise there is a considerable probability that polymerization will take place in an emulsified monomer phase without involving the rubber, resulting in an intimate rubber-polymer mixture rather than a rubber-polymer compound.

In the analogous case of solvent imbibed by synthetic polymer in an emulsion system, it is generally believed that, in the absence of an excess of solvent-solubilizing soap micelles, equilibrium is established rapidly. Thus a polystyrene latex of average particle diameter 0.08μ has been shown to reach equilibrium with toluene within 30 minutes³. A rate of polymerization sufficiently rapid to outstrip this rate of solution would not generally be encountered. It can, accordingly, be assumed that the polystyrene-latex particles are maintained in a state of equilibrium solubility with regard to any free monomer phase present, and that the monomer-polymer ratio in the particles during polymerization is maintained by this equilibrium solubility as long as a free monomer phase exists.

In Hevea latex the rubber particles have an average size about ten times greater than that of the above polystyrene latex particles, with a broad distribution of particle size. Under conditions recently recommended⁴ for polymerizing methyl methacrylate or styrene in natural-rubber latex, the polymerization is left to proceed quite rapidly, and with methyl methacrylate it is already fairly complete within 30 minutes of adding the initiator. This rate is probably sufficiently rapid to outstrip the rate of imbibing monomer from any excess dispersed in the serum. It is, therefore, essential that the rubber parti-

* Reprinted from the *Journal of Applied Chemistry*, Vol. 5, pages 609-615, November 1955.

cles absorb as much of the monomer as possible before polymerization is started. A study has accordingly been undertaken to determine when equilibrium is obtained with rubber latex and methyl methacrylate, as a guide to the more general behavior of latex-monomer systems. The limited solubility of methyl methacrylate in rubber assists the present study since a separately emulsified monomer phase is more easily obtained compared with monomers which are more miscible with rubber, e.g., styrene.

EXPERIMENTAL

MISCIBILITY OF METHYL METHACRYLATE WITH RUBBER LATEX

When methyl methacrylate in amount not exceeding its solubility limit in rubber is stirred into unstabilized Hevea latex, it first tends to separate into an upper layer, but fairly rapidly disappears as a separate liquid phase, and soon afterwards no visible separation of monomer occurs on standing. This mixing process is usually complete, as judged visually, within 10-15 minutes, and is expedited by shaking. On prolonged standing some partial creaming occurs and much later the creamed layer gels. The use of such an unstabilized latex is confined to relatively small-scale mixing. On a larger scale the pool of liquid monomer disperses more slowly, and there is sufficient time for clotting and partial coagulation of the latex in contact with the monomer pool. With the addition to the latex of a stabilizer (ammonium caseinate, oleate, stearate or a nonionic polyethylene oxide condensate) dispersion of monomer is achieved more easily and without pre-coagulation, and if the stabilizer is formed *in situ* by adding oleic or stearic acid to the monomer and stirring the mixture into ammoniated latex a smooth dispersion is obtained. Smooth mixing also occurs with already emulsified monomer. In the presence of stabilizer, a proportion of monomer substantially exceeding the solubility limit of monomer in rubber can be incorporated without the physical separation of a monomer layer as occurs with similar proportions of monomer in an unstabilized latex.

POLYMERIZATION TECHNIQUES

[†] The procedure⁴ already referred to gives high conversions of methyl methacrylate and styrene in natural-rubber latex. Using a commercial methyl methacrylate (Kallodoc) containing 0.01 per cent of hydroquinone it is unnecessary to remove the inhibitor, but at the 0.1 per cent hydroquinone level more generally used in commercial monomer its removal is essential.

The choice of stabilizer for the latex is influenced by the end-usage of the product; thus for electrical applications ammonium stearate is preferred to other soaps, casein, or polyethylene oxide. For other applications ammonium oleate is a particularly effective stabilizer. To minimize the likelihood of polymerizing some of the monomer in a separately emulsified phase the amount of stabilizer should be kept to a minimum, and with ammonium oleate 0.5 per cent on the rubber is adequate. If the proportion of stabilizer is substantially increased and especially if the monomer is emulsified prior to its addition to latex, much of the monomer polymerizes independently of the rubber. Advantage has been taken of this fact in polymerizing vinyl acetate in rubber latex. The presence of rubber or any other polyisoprene so greatly retards the polymerization of vinyl acetate⁵ that it is impracticable to polymerize this monomer when dissolved in rubber. Hence there is little prospect of obtaining a rubber-polyvinyl acetate compound in this way. By emulsifying the vinyl acetate in

rubber latex it can be polymerized independently of the rubber to give an intimate rubber-polyvinyl acetate mixture⁶.

Persulfates, perborates, hydrogen peroxide, alkyl hydroperoxides, benzoyl peroxide, reduction-activated organic hydroperoxides, diazoaminobenzene, diazothioethers, diazonium salts and azobis-isobutyronitrile have all been used to initiate polymerization of vinyl monomers in natural-rubber latex. Very high conversions at moderate temperatures have been obtained with reduction-activated hydroperoxides, and polyethylene-polyamine activated hydroperoxides are especially suitable, since they do not require deamination of the latex nor are they particularly sensitive to inhibition by oxygen. *tert*-Butyl and cumene hydroperoxides with triethylenetetramine or tetraethylenepentamine have been found to give rather better results than more active hydroperoxides such as those of *p*-menthane, di-isopropylbenzene, or phenylcyclohexane. A trace of soluble iron is an essential part of a polyamine-activated hydroperoxide recipe, and commercial latex concentrate usually contains sufficient iron for this purpose. Occasionally, however, it has been found necessary to add a trace of iron, and 5 p.p.m. added as ferrous sulfate has been adequate. It has also been found essential to add a similar amount of an iron salt to fresh field latex or to purified latex.

Rubber has a retarding effect on polymerization of most vinyl monomers⁷, and in latex there is a contributory retardation due to nonrubber substances. Consequently a substantially higher proportion of initiator to monomer is necessary compared with a conventional emulsion polymerization system. To counteract the various retarding influences which increase as the ratio of rubber to monomer is increased, the amount of initiator is based on the rubber content of the latex, irrespective of the proportion of rubber to monomer. Rather different proportions of initiator are required by the different monomers listed in Table I.

Acrylonitrile and vinylidene chloride cannot be used with amine activation in rubber latex, but they have been successfully polymerized using dihydroxyacetone-ferrous iron activation of *tert*-butyl hydroperoxide⁸. Acrylonitrile has also been polymerized in rubber latex using other peroxidic initiators, and the addition of benzene has been found helpful in obtaining some apparent rubber-polymer combination⁹. Acrylic acid is a coagulant for rubber latex, but it has been pre-emulsified, mixed with latex, and polymerized with the aid of a diazo-initiator⁹.

CHARACTERIZATION OF POLYMER-MODIFIED LATEX

Owing to the very considerable difference in size between the larger rubber particles in Hevea latex and the uniformly small particles in a synthetic polymer emulsion, it becomes feasible to examine the reacted latexes in three ways, viz.:

(1) Electron micrographs of material prepared from a Hevea latex fraction of large particle size should reveal the presence of any separately formed polymethyl methacrylate particles.

(2) Physical separation of any free polymer particles should be possible by selective creaming.

(3) Fractionation of polymer-modified latex according to particle size or density should reveal any heterogeneity resulting from preferential reaction with smaller particles or from formation of separately-emulsified polymer.

Additionally, a separative procedure based on fractional precipitation from solution can be applied to cast film or coagulum obtained from the modified

TABLE I
POLYMERIZATION RECIPES FOR VARIOUS MONOMERS

Monomers	Initiator (parts per 100 parts of rubber)		Conditions
	Hydroperoxide ^(a)	Amine ^(b)	
Methacrylates	0.2	0.2	Room temperature (exothermic)
Acrylates ^(c)	0.3	0.35	6 hours at 60°
Styrene	0.25	0.1	6 hours at 55°
Acrylamide ^(d)	0.2	0.2	Room temperature (exothermic)
Vinylpyridine ^(d)	0.2	0.2	Room temperature (exothermic)

(a) *tert*-Butyl or cumene hydroperoxide.

(b) Tetraethylenepentamine.

(c) F. J. Popham, unpublished results.

(d) G. P. McSweeney, unpublished results.

latex¹⁰. This, however, only gives an overall estimate of the amounts of polymer bound to rubber and present in the free state, and cannot differentiate between free polymer formed inside the latex particles and that formed in a separate emulsion system.

A latex fraction of large particle size is easily obtained by fractional creaming if the latex is diluted with at least 10 volumes of 0.01–0.02 per cent ammonium alginate solution containing 0.5 per cent ammonia¹¹. Three subsequent creamings from 0.02 per cent ammonium alginate effectively remove any remaining small particles, and an electron micrograph¹² of such a fraction is reproduced in Figure 1. Figure 2 shows the same latex after polymerization of 20 per cent of methyl methacrylate on the weight of rubber, and no small particles of separately formed polymer can be seen.

Polymethyl methacrylate has a specific gravity greater than unity. Consequently if the large-particle latex is mixed with polymethyl methacrylate emulsion and recreamd from 0.02 per cent alginate, the larger and lighter rubber particles rise to the surface while the polymer particles remain in the serum. Quantitative separation of the rubber and polymer has been achieved in this way, whereas if the rubber-polymer latex mixture is coagulated and dried, the two components are no longer completely separable by fractional precipitation

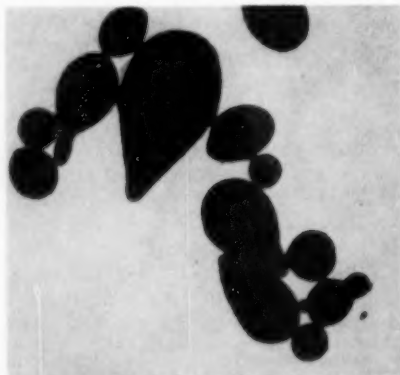


FIG. 1.—Large particle latex fraction, magnification 6,000 X.

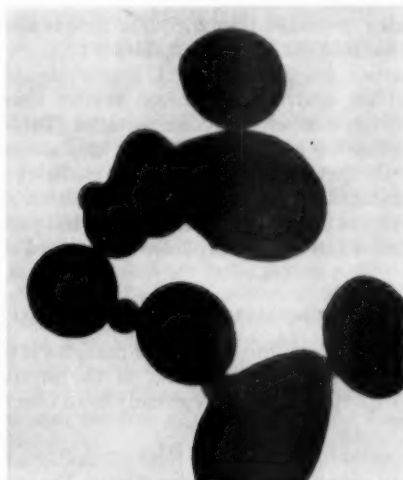


FIG. 2.—Large particle latex fraction after polymerizing methyl methacrylate therein; magnification 12,500 \times .

from solution. The creaming method is, therefore, eminently suitable for separating any free emulsion-polymer particles from a rubber latex in which a monomer has been polymerized. Table II clearly shows that no monomer is polymerized in a separately emulsified phase, even when using the largest

TABLE II
LARGE-PARTICLE HEVEA LATEX: EFFECT OF TIME OF CONTACT OF METHYL METHACRYLATE (MM) WITH RUBBER BEFORE INITIATING POLYMERIZATION, USING 1 PER CENT AMMONIUM OLEATE ON RUBBER; PEROXAMINE RECIFE

	Time of contact before polymerization					
	20 min.	20 min.	20 min.	2 hrs.	6 hrs.	20 hrs.
Wt of rubber in latex (g.)	7.1	16.4	16.4	17.3	17.6	16.7
Wt. of monomer added (g.)	2.3	7.5	11.8	7.5	7.5	7.5
Poly-MM isolated from creamed serum:						
Weight (g.)	0.55	1.76	4.7	1.4	0.13	Nil
Analysis: C, %	62.0	60.4	60.65	60.4		
H, %	8.1	8.1	8.1	8.15		
$[\eta]$	0.44	0.36	0.54	0.43		
Mol. wt.	88,000	70,000	120,000	88,000		
Polymer-modified rubber isolated from cream:						
Weight (g.)	8.8	21.45	22.25	23.0	24.5	23.6
Polymer content (%)*	19	24	28	25	30	30
Total poly-MM accounted for (g.)						
	2.2	6.8	10.55	7.0	6.6	6.9
% conversion calculated	95	91	89	93	97	92
% of polymer formed in rubber phase	76	75	55	80	97	100
in serum	24	25	45	20	3	0

* Estimated from oxygen content.

particles of Hevea latex, provided that adequate time is allowed for the methyl methacrylate to diffuse into the rubber particles.

The very large particle fraction of Table II represents only about 10 per cent by weight of the rubber, and the very much shorter time required to reach equilibrium shown by the somewhat smaller particles (Table III) indicates that 1-2 hours should suffice for adequate diffusion into an unfractionated latex. This is confirmed by the fact that no free polymer particles can be isolated from the creamed or centrifuged serum of a total Hevea latex after polymerization therein of up to 40 parts of methyl methacrylate per 100 parts of rubber. Even higher levels of monomer can be used provided that added stabilizer is kept to a minimum.

HETEROGENEITY OF MODIFIED LATEX

Where diffusion of a reagent into the rubber particles is the rate-determining step in a latex reaction some heterogeneity of the product with respect to particle size is to be expected. This has already been observed in the addition

TABLE III
MEDIUM-LARGE-PARTICLE LATEX (SECOND CREAM FRACTION). EFFECT OF
TIME OF CONTACT AND STABILIZER CONCENTRATION ON METHYL
METHACRYLATE POLYMERIZATION IN NATURAL-RUBBER LATEX

Monomer added (parts per 100 parts of rubber)	Ammonium oleate (% on rubber)	Time of contact	% of polymer formed		Total conversion (%)
			in rubber	in serum	
45	0.5	20 min.	95	5	91
45	0.5	2 hrs.	100	Nil	93
45	0.5	6 hrs.	100	Nil	93
45	1.0	1 hr.	93	7	90
45	Nil	1 hr.	100	Nil	94
67	1.0	1 hr.	88	12	91
67	0.5	2 hrs.	98	~ 2	93
100	1.0	1 hrs.	80	20	90
100	0.5	1 hrs.	95	5	91
100	0.5	2 hrs.	97	~ 3	92

of hydrogen chloride to rubber in latex¹³ and in the acid-catalyzed cyclization of latex¹⁴. Fractionation of a methyl methacrylate-modified latex, both by creaming and centrifuging, has also revealed considerable heterogeneity even when sufficient time is allowed for the rubber and monomer to attain equilibrium¹⁵. Higher proportions of polymer are found in the smaller particles than in the larger ones, and it therefore seems likely that the smaller rubber particles are the more favored loci for monomer-polymerizations in Hevea latex.

CONCLUSIONS

High conversions of vinyl monomers to polymers can be obtained in natural-rubber latex using activated initiating systems at moderate temperatures. High proportions of surface-active stabilizers favor polymerization of the vinyl monomer, independently of the rubber phase, to give a rubber-polymer mixture. With a low proportion of stabilizer, and allowing adequate time for diffusion of monomer into the rubber, most of the polymerization occurs within the swollen rubber particles, thus favoring combination of polymer and rubber when using suitably chosen monomers and initiators.

APPENDIX

EXPERIMENTAL TECHNIQUE

PARTICLE-SIZE FRACTIONATION OF LATEX

To commercial latex concentrate (500 ml.) was added ammonium oleate (6 g.) to displace nonrubber substances so as to avoid gross contamination of the smaller particle fractions. Water (4100 ml.), aqueous ammonia (100 ml., d. 0.880) and 1 per cent ammonium alginate solution (70 ml.) were added, and the latex was set aside to cream for 4 days to give the first cream fraction of large particle size. The lower serum was run off and its ammonium alginate concentration was raised to 0.025 per cent, giving a second cream fraction of medium-large particle size. The alginate content of the serum was next raised to 0.05 per cent, giving a third cream fraction of intermediate particle size, and finally to 0.2 per cent which effectively creamed all the remaining rubber particles. Each creamed fraction was again creamed three times from alginate solutions of appropriate concentration (i.e., 0.02, 0.03, 0.06, and 0.25 per cent, respectively). Two latex samples so treated gave the following fractions:

Fraction % of total rubber in the fraction:

	Centrifuged concentrate	Electrodecanted latex
1st cream	10	17.5 (N, 0.04%; O, 0.41%)
2nd cream	53	42 (N, 0.03%; O, 0.43%)
3rd cream	17	17 (N, 0.04%; O, 0.58%)
4th cream	20	23.5 (N, 0.07%; O, 1.35%)

POLYMERIZATION OF METHYL METHACRYLATE IN RUBBER-LATEX FRACTIONS

The latex was diluted with water so that the final solids content would not exceed 55 per cent and the required amount of ammonium oleate was added as a 2 per cent solution. Ferrous sulfate was added to give 5-10 p.p.m. of ferrous iron in the aqueous phase. Methyl methacrylate was stirred into the latex for the times indicated in Table II, and then the initiator was added, using the amounts shown in Table I. For polymerizations started within 2 hours of mixing, the hydroperoxide was conveniently added to the monomer and only the amine was added (in 10 per cent solution) to initiate the polymerization. In the 6-hour and 20-hour experiments, both the hydroperoxide and the amine were added successively after the times indicated. Rapid exothermic polymerization occurred within 10-15 minutes, after keeping overnight the latex was diluted with 0.02 per cent ammonium alginate solution and left to cream. Polymethyl methacrylate was recovered from the serum by heating to 100° and adding excess of hydrochloric acid together with a little calcium chloride, and was purified by extraction with methanol, dissolving in benzene, centrifuging out alginic acid and freeze-drying. The polymer-modified rubber was isolated as a crumb by pouring the cream into three times its volume of 0.5 per cent formic acid at boiling point.

GENERALIZED PROCEDURE FOR POLYMERIZATION OF METHYL METHACRYLATE IN NATURAL-RUBBER LATEX

To commercial ammoniated rubber latex of 60 per cent rubber content is added an equal volume of water together with sufficient ammonium oleate to provide 0.5 per cent on the rubber. Into this is stirred the required amount of

methyl methacrylate (containing not more than 0.01 per cent hydroquinone) to which has been added an amount of *tert.*-butyl or cumene hydroperoxide calculated on the basis of 0.2 parts per 100 parts of rubber in the latex. After setting aside for 2 hours a similar amount of tetraethylenepentamine (as a 10 per cent solution) is stirred in. Stirring is then stopped and the reaction vessel is covered; provided it is reasonably full, no additional precautions are necessary to exclude air. Polymerization should be substantially complete within 2 hours, during which there is a rise of temperature. The product is then isolated by running the latex into at least three times its volume of boiling water containing 0.5 per cent of formic acid, the resulting crumb being easily filtered or centrifuged, washed, dried, and sheeted on a rubber mill.

Certain other monomers may be substituted for methyl methacrylate, using the modifications indicated in Table I.

SUMMARY

Practical methods are described for polymerizing methacrylic esters, styrene, and other vinyl monomers in natural-rubber latex. The larger rubber particles require an appreciable time to attain equilibrium with the monomer diffusing into them from a liquid monomer phase dispersed in the serum. Provided that substantial proportions of added surface-active substances are avoided, rubber-soluble monomers can be polymerized almost entirely within the rubber particles, and the modified latex then contains no separately emulsified free polymer. Such conditions favor combination of polymer with rubber. The addition of a sufficiently large amount of dispersing agent favors polymerization of emulsified monomer, with less involvement of the rubber. In this way there can be obtained mixtures of rubber and polymer from monomers whose polymerization is otherwise inhibited by the presence of polyisoprene hydrocarbons.

ACKNOWLEDGMENTS

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MASTICATION. PART III. CHEMICAL VERIFICATION OF THE MECHANICAL DEGRADATION MECHANISM OF COLD MASTICATION *

G. AYREY, C. G. MOORE, AND W. F. WATSON

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
WELWYN GARDEN CITY, HERTFORDSHIRE, ENGLAND

The plasticization of natural and synthetic rubbers by cold mastication results from the degradation of the macromolecules. In Part I¹ experimental evidence was presented that such degradation is caused by mechanical rupture of primary carbon-carbon bonds in the polymer (R—R) to give polymer radicals (R·) which are stabilized by oxygen to give degraded polymer molecules. Such a mechanism, invoking mechanical shear, had been advocated previously, e.g., by Staudinger², most explicitly by Kauzmann and Eyring³, but required systematic mastICATIONS under nitrogen with a large variety of compounds (radical acceptors) to demonstrate more critically its consistency with experimental observations⁴.

However, Part I provided no direct chemical evidence supporting the mechanism by demonstrating reaction between the rubber radical and radical-acceptor molecule. Considering that only of the order of 0.1 per cent of radical acceptor is required for radical termination to give marked degradation, especially favorable reactions and sensitive analytical techniques are required for detecting the basic chemical reactions.

The incorporation of radical acceptors into two types of elastomer on mastication has been demonstrated by the use of two radical-acceptor molecules and two distinct analytical techniques: (1) the incorporation of 1,1-diphenyl-2-picryl hydrazyl into natural rubber, using a spectrometric method, and (2) the incorporation of 1,1'-dinaphthyl [S³⁵]-disulfide into GR-S, using a radiochemical method. The incorporation of the radical acceptors should be correlated with extent of degradation measured by decrease in molecular weight. Quantitative correlations have been obtained for both the above radical acceptors.

1,1-DIPHENYL-2-PICRYL HYDRAZYL

This stable free radical was chosen because (a) it is probably incorporated in the rubber on mastication by direct coupling:



(b) it is one of the most reactive of the radical acceptors reported¹, and (c) its intense color allows spectroscopic determinations of concentration in dilute solution.

EXPERIMENTAL METHODS AND MATERIALS

1,1-Diphenyl-2-picryl hydrazyl (DPPH).—DPPH was prepared by oxidation of the hydrazine in benzene solution by lead oxide⁵. Benzene was re-

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moved from the 1,1 addition complex by heating in vacuo at 80° C while condensing the benzene evolved by liquid oxygen, to give the hydrazyl, m.p. 137° C of analysis: C, 54.8%; H, 3.1%; O (direct), 23.8%; *M* (ebull., benzene) 400. Calculated: C, 54.7%; H, 3.3%; O, 24.3%; *M* 394.

Natural rubber.—Deproteinized crepe of N < 0.1%, O < 0.5%, gel < 1%, acetone extract 1.5%, was kindly supplied by Dr. van der Bie of Indonesian Rubber Research Institute (J. P. P. Karet). Without purification, it caused marked decomposition of DPPH in solution in benzene and after freeze-drying. Cold extraction by several batches of acetone proved effective in eliminating this spurious decomposition which occurred in benzene in vacuo and on freeze-drying. Figure 1 shows the similarity of absorption spectrum of the pigment recovered from the extracted rubber with that of the initial DPPH.

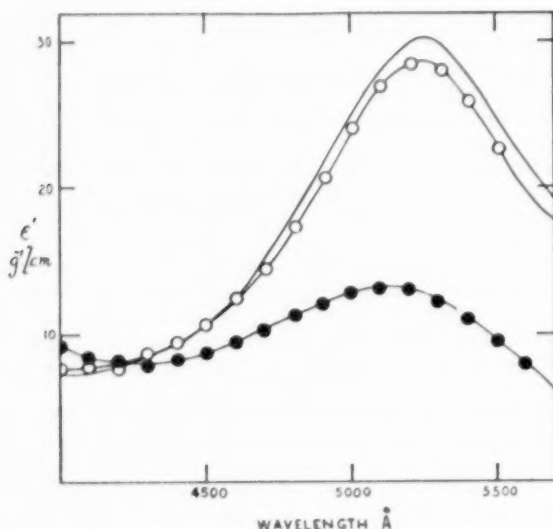


Fig. 1.—Recovery of DPPH from rubber: (—) DPPH in acetone; (○) DPPH recovered from freeze-dried rubber; (●) DPPH recovered from rubber after 10 min. mastication under nitrogen.

Mastication.—Mixtures of rubber-DPPH were prepared by freeze-drying. 0.87 g. samples were masticated in a laboratory internal masticator⁶ with a chamber volume of 1.3 ml. The masticator was flushed with nitrogen for 5 minutes and a positive pressure of 10 mm. Hg maintained within the chamber during mastication. The masticated sample was divided into two parts, one for determination of molecular weight and the other for determination of uncombined DPPH.

Molecular weight determination.—Intrinsic viscosities in benzene at 25° C were obtained by linear extrapolation of reduced viscosity vs. concentration for three concentrations in the range 0.3–0.1 g./100 ml. using B.S.S. 1 viscometers. A calibration of viscosity number with osmotic molecular weights for masticated natural rubbers enabled conversion to number-average molecular weights⁶.

Determination of uncombined DPPH.—The masticated rubber sample (~0.5 g.) was dissolved in 10 ml. benzene in vacuo. (Oxidation of the rubber

during dissolution caused DPPH decomposition.) The rubber was precipitated by ~ 240 ml. acetone to make up to a standard volume of 250 ml. Suspended rubber was removed by centrifuging for 1 hour at 20,000 g. Although this solution contained unchanged DPPH from freeze-dried mixtures with rubber, the DPPH in the acetone solution after masticating was partly decomposed other than by reaction with rubber free radicals (Figure 1) even with extracted rubber. Fortunately, DPPH and the product formed by this spurious reaction could both be reduced and determined as the hydrazine by the simple reduction method outlined below.

Excess of hydroquinone was added to the centrifuged acetone solution to reduce the DPPH to hydrazine within a few hours. After standing overnight, sulfur dioxide was bubbled into the solution for 30 seconds to effect a rapid change of color from orange to the characteristic yellow color of the hydrazine.

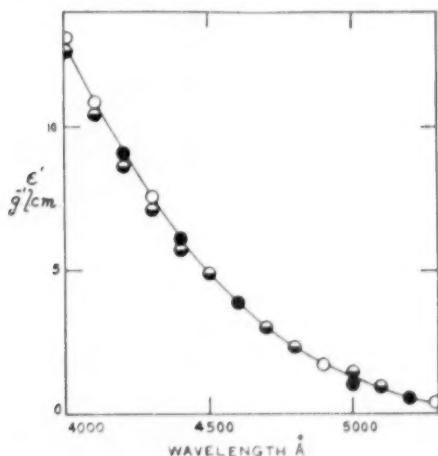


Fig. 2.—Spectra after reduction of DPPH recovered from rubber: (full curve) Reduction of DPPH in acetone; (○, ●) reduction of DPPH, of $\epsilon'_{4350} = 28.6$ and $25.5 \text{ g.}^{-1} \text{ l. cm.}^{-1}$, respectively, recovered from freeze-dried rubber; (●) reduction of DPPH of $\epsilon'_{4350} = 17.5 \text{ g.}^{-1} \text{ l. cm.}^{-1}$ recovered from rubber after mastication.

Varying the amounts of hydroquinone or sulfur dioxide, or times of standing, caused no change in spectrum. Extracts of partly decomposed DPPH after reduction gave identical spectra to that of DPPH added to acetone and reduced by the two reductants (Figure 2).

Spectra were measured by a Hilgar Uvispec spectrophotometer. In all cases, extinction coefficients, ϵ , are expressed in units of g. initial DPPH/l. solution/cm. When some of the DPPH is combined with the rubber, the above choice of units gives apparent extinction coefficients ϵ' . By Beer's law, ϵ'/ϵ gives the fraction of DPPH recovered.

EXPERIMENTAL RESULTS

Preliminary experiments showed that spectra identical in shape with that in Figure 2 were obtained from several concentrations of DPPH in rubber after varying extents of mastication, and that absorption was proportionately less throughout the wave length range measured, indicating incorporation of frac-

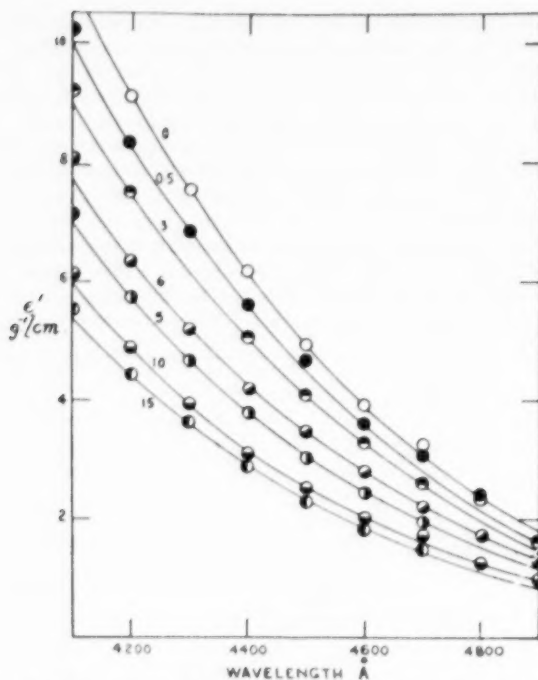


Fig. 3.—Spectra of reduced DPPH recovered from masticated rubber. The numbers of the curves give the periods of mastication in minutes.

tions of the DPPH by the rubber. For quantitative comparison of DPPH combined with the rubber and that calculated from decrease in molecular weight, a stock mixture of 0.1176 g. DPPH in 10.004 g. rubber was prepared by freeze-drying from benzene solution. Samples were masticated from 0.5 to 15 minutes, under nitrogen. Figure 3 records the spectral properties of the recovered hydrazine. The curves are spectra calculated from that of Figure 2 on adjustment for DPPH combined with rubber by coincidence with the measured ap-

TABLE I
CHEMICAL DETERMINATION AND PHYSICAL ESTIMATES OF DPPH
COMBINED WITH NATURAL RUBBER ON MASTICATION

Minutes masti- cation	Chemical detn. of DPPH in rubber		[η]	\bar{M}_n ($\times 10^{-3}$)	Physical estimate of DPPH in rubber, mole/g. ($\times 10^3$)
	%	Mole/g. ($\times 10^3$)			
0	—	—	2.88	3.09	—
0.5	9	0.26	2.22	2.34	0.21
3	17	0.50	1.30	1.40	0.78
4	28	0.83	1.13	1.23	0.98
5	36	1.06	1.05	1.13	1.12
6	29	0.87	1.02	1.11	1.16
10	46	1.37	0.85	.85	1.50
15	50	1.50	0.81	.89	1.60

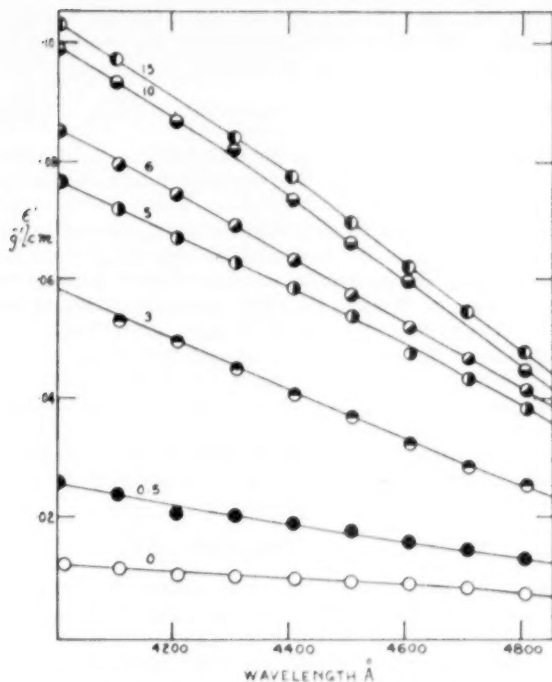


FIG. 4.—Spectra of rubbers after mastication with DPPH.

parent absorption coefficient at 4200 Å. Agreement with extinction coefficients at other wave lengths is within experimental error. The decrease in apparent extinction coefficients at 4200 Å. gives the amounts of DPPH incorporated in the rubber recorded in Table I, column 3.

Table I also records the viscosities of the masticated rubbers and the equivalent number-average molecular weights. From these physical measurements, the moles of new chains per gram rubber, m , is given by:

$$m = (1/\bar{M}_{n,m} - 1/\bar{M}_{n,0}) \quad (1)$$

TABLE II
COLORATION OF RUBBER ON MASTICATION WITH DPPH

Minutes mastication	Absorption at 4200 Å., g. ⁻¹ l. cm. ⁻¹ ($\times 10^3$)	Absorption at 4200 Å. rel. to that of rubber after 15 min. mastication with DPPH	
		Chemical detn.	Physical est.
0	1.21	—	—
0.5	2.09	0.11	0.13
3	5.05	0.47	0.49
4	5.71	0.55	0.61
5	6.62	0.66	0.70
6	7.54	0.77	0.73
10	8.75	0.92	0.94
15	9.43	—	—

where $\bar{M}_{n,0}$ and $\bar{M}_{n,m}$ are the number-average molecular weights before and after mastication. As two molecules of DPPH are combined for each new chain produced, the amount of DPPH combined is given by:

$$\text{moles DPPH combined/g. polymer} = 2(1/\bar{M}_{n,m} - 1/\bar{M}_{n,0}) \quad (2)$$

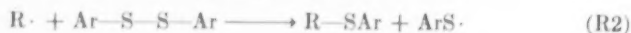
The physical estimates are given in Table I, column 6. Columns 3 and 6 provide good agreement between the chemical determination and physical estimates of DPPH combined.

The rubber after removal of uncombined DPPH was colored. After three precipitations from benzene by methanol, freeze-drying, cold extraction by methanol, and drying, the absorption spectra of the masticated rubbers were measured in chloroform (Figure 4). The relative extents of coloration are consistent with expectations from extent of degradation (Table II). Subtracting the absorption of the unmasticated sample from those of the masticated samples, the resultant coloration produced by mastication gives absorptions compared with that of the most degraded sample, which are similar to the relative amounts of DPPH estimated to be combined from Table I, column 6.

Conclusion.—DPPH is combined with rubber in amounts predicted by the mechanical degradation mechanism. This is supported by the increase in color of the rubber with extent of mastication.

1,1'-DINAPHTHYL DISULFIDE

1,1'-Dinaphthyl disulfide was chosen as the radical acceptor for the following reasons: (1) aromatic disulfides are effective plasticizing agents in the cold mastication of natural rubber in nitrogen¹; (2) the disulfide probably reacts with a rubber radical according to (R2) and (R3) resulting in the incorporation of sulfonyl radicals ($\text{ArS}\cdot$) in the degraded polymer;



(3) of several aryl disulfides investigated it was found to be the most efficient in promoting breakdown; (4) it is readily synthesized with isotopically labelled sulfur atoms by the reaction of elementary $[\text{S}^{32}]$ with 1-naphthyl-magnesium bromide to give 1-naphthyl- $[\text{S}^{32}]$ -thiol, which is subsequently oxidized to 1,1'-dinaphthyl $[\text{S}^{32}]$ -disulfide, uniformly labelled in both sulfur atoms.

EXPERIMENTAL METHOD AND MATERIALS

Preparation of materials.—(1) *Inactive 1,1'-dinaphthyl disulfide.* Oxidation of 1-naphthylthiol (b.p. $84^\circ/0.03$ mm., n_D^{20} 1.6814), in aqueous sodium hydroxide, with an equimolar amount of 30 per cent hydrogen peroxide at -10° gave the disulfide (85 per cent yield), which after four recrystallizations from ethanol had m.p. $88-89^\circ$ (found: C, 75.6; H, 4.45; S, 20.0; Calculated for $\text{C}_{20}\text{H}_{14}\text{S}_2$: C, 75.45; H, 4.4; S, 20.15).

(2) *1,1'-Dinaphthyl $[\text{S}^{32}]$ -disulfide.* A small-scale synthesis of the disulfide was conducted in four stages: (1) *Preparation of 1-naphthyl-magnesium bromide.* A solution of this compound was prepared by the method⁷ of Gilman *et al.*, from magnesium (0.025 gram atom) and 1-naphthyl bromide (0.024 gram mole), and assayed by the acid titration method⁸ of Gilman *et al.*, using screened methyl red as indicator. (2) *Reaction of $[\text{S}^{32}]$ with Grignard reagent.* The

Grignard reagent (3.0 millimole) was pipetted into tube A of Figure 5, ether added to make the volume up to 10 ml., and the apparatus flooded with nitrogen. Elemental [S^{35}] (63 mg., 1.97 millimole, 6.3 mc., supplied by Radiochemical Center, Amersham, England), in xylene (5.0 ml.) was slowly added (30 minutes) from B to the Grignard reagent at 0° , the reactants being stirred by a nitrogen stream. The liquid air trap C served as a protection against moisture. The bulb D acted as a liquid trap in case of a blow back due to pressure build up in a series of aqueous sodium hydroxide traps connected at E. Reaction was completed by standing at 0° for one hour, followed by gently refluxing the solution for a further hour.

Decomposition of the product was effected at -15° by slow addition of 15 per cent hydrochloric acid (1.0 ml.) followed by water (4.0 ml.). (3) *Extrac-*

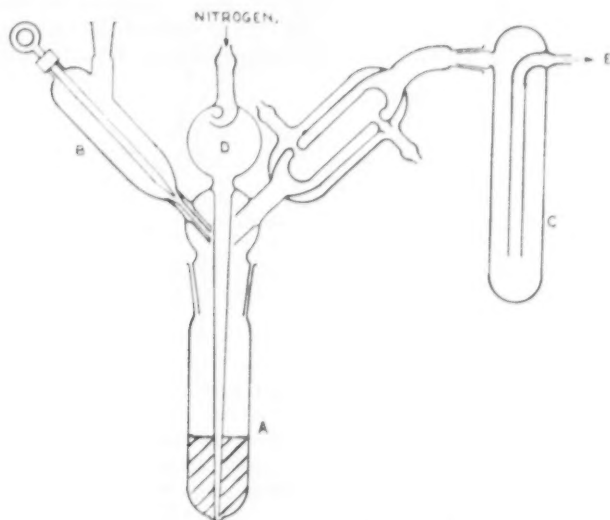


FIG. 5.—Apparatus for preparation of 1-naphthyl- $[S^{35}]$ -thiol.

tion of the 1-naphthyl- $[S^{35}]$ -thiol. The tube A was rapidly transferred to the extraction apparatus (Figure 6), which is a modification of that described by Collins⁹. The extraction was conducted under an atmosphere of nitrogen. By suitable adjustment of taps, the two layers were transferred to the separating funnel G, the aqueous layer returned to A, and the organic layer transferred to F. The aqueous layer was returned to G, extracted with ether (2×3 ml.), added through H, and the combined ether fractions transferred to F. Agitation of the two phases in G was by means of a magnetic stirrer I. By a similar procedure, the $[S^{35}]$ -thiol in the organic layer was extracted with 10 per cent aqueous sodium hydroxide (3.0 ml., $+ 2 \times 1.5$ ml.), the aqueous alkaline solution washed with ether (5 ml.) and then transferred to the flask of Figure 7. (4) *Oxidation of the $[S^{35}]$ -thiol.* The aqueous sodium salt of the thiol was oxidized at ca. 0° with 30 per cent hydrogen peroxide (0.1 ml.) in the flask of Figure 7. After standing for 24 hours at room temperature, the aqueous phase was removed through the filter at J, the solid $[S^{35}]$ -disulfide washed repeatedly

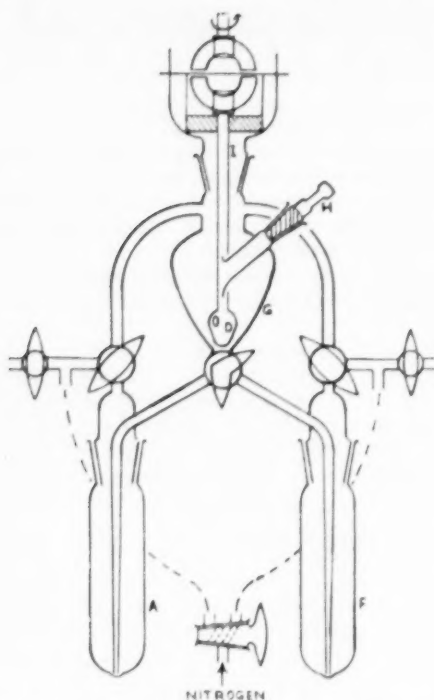


FIG. 6.—Apparatus for isolation of 1-naphthyl-[S³⁵]-thiol.

with water (10 ml.) and finally dried in vacuo to constant weight (yield, 239 mg., 76 per cent). Trial syntheses with inactive sulfur gave over-all yields of 75–80 per cent of substantially pure disulfide, m.p. 87–88°, mixed m.p. with authentic sample 87.5–88.5° (*found*: C, 75.2; H, 4.4; S, 20.05). The [S³⁵]-disulfide was dissolved in ethanol and equilibrated under gentle reflux with pure inactive disulfide (1.705 g.). After three crystallizations from ethanol in a flask of Figure 7 a pure [S³⁵]-disulfide (1.723 g.) (*found*: S, 20.1) was obtained; this is designated [S³⁵]-disulfide I. This material, when counted as an infinitely thick layer of benzidine sulfate (see below), had a corrected count rate of 2.25×10^6 counts/minute. The radiochemical purity of this material was shown to

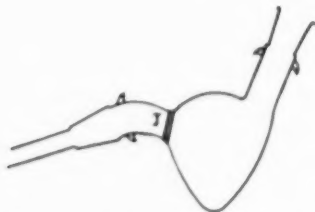


FIG. 7.—Apparatus for oxidation of 1-naphthyl-[S³⁵]-thiol to the [S³⁵]-disulfide.

be > 97.5 per cent by the following dilution experiments. First, $[S^{35}]$ -disulfide I (0.1679 g.) was equilibrated in ethanolic solution with pure inactive disulfide (1.995 g.) and the mixed disulfides recrystallized five times from ethanol (40 ml. per time) to give $[S^{35}]$ -disulfide II (1.728 g.). Second, $[S^{35}]$ -disulfide I (0.05527 g.) was equilibrated in petroleum ether (b.p. 60–80°) with pure inactive disulfide (2.602 g.) and the mixed disulfides recrystallized five times from petroleum ether (30 ml. per time) to give $[S^{35}]$ -disulfide III (1.590 g.). The observed and calculated activities of the diluted $[S^{35}]$ -disulfides are given in Table III as count rates of "infinitely thick" benzidine sulfate samples counted under standard conditions; the calculated activity is obtained by multiplying the activity of $[S^{35}]$ -disulfide I by the appropriate dilution factor.

(3) *Polymer*. Polysar S-50 GR-S was purified by hot acetone extraction followed by repeated fractional precipitation from benzene solutions by means of methanol and ethanol. A middle fraction of the polymer (*found*: O, 0.12; N, 0.01; S, <0.1) was stored as a 1.5 per cent solution in benzene, under nitrogen in the dark. During seven months storage the intrinsic viscosity, $[\eta] = 2.32$ 100 ml./g. in benzene at 25°, showed no change.

TABLE III
 $[S^{35}]$ -DISULFIDE ACTIVITY AS BENZIDINE SULFATE

Sample	Counts/min.	
	Observed	Calculated
I	2.25×10^4	—
II	1.76×10^4	1.75×10^4
III	4.57×10^4	4.68×10^4

Assay of samples for $[S^{35}]$.—(1) The activities of "infinitely thick" samples were determined with a G.E.C. mica end-window Geiger-Müller counter (type E.H.M. 2S). With high activity samples sufficient counts were taken to give a standard error of less than ± 1 per cent. With samples having activities of less than 100 counts/minute, sufficient counts were taken to give a standard error of less than ± 3 per cent. All count rates recorded have been corrected for the resolving time of the counter, background, variations in counter efficiency, decay, and sample dilution.

(2) *Assay as benzidine sulfate*. The method of Ayrey, Barnard, and Moore¹⁰ was used.

(3) *Assay as polymer films*. 2 per cent solutions of the active polymer in benzene were filtered into aluminum trays supported on glass plates that floated on mercury in an airtight box. The samples were evaporated to dryness under nitrogen at 50–60° and final drying effected in vacuo. The volumes of polymer solutions were adjusted to give "infinitely thick" polymer films of 0.2 mm. thickness (20 mg./cm.²). This value was shown by independent experiment to be in the "infinite thickness" range for the β -radiation of $[S^{35}]$ (cf. Walling¹¹). Circular disks (3.5 cm. diameter) of the polymer film on the aluminum support were cut out from the trays, mounted in a brass cup, masked with a stainless steel washer (1.8 cm. internal diameter) and placed under conditions of reproducible geometry below the counter window. Using the above technique and standard solutions of $[S^{35}]$ -disulfide I and GR-S in benzene a calibration curve (Figure 8) was obtained relating count rate to the weight of $[S^{35}]$ -disulfide 1/g. of polymer. Three polymer films were assayed for each concentration and the mean count rate recorded. The best straight line through the

origin had a slope 2.98×10^6 with standard deviation 0.02×10^6 and the standard deviation of the single points was 3.3 per cent, giving a probable error of 2.3 per cent in the determination of the weight of disulfide.

Determination of molecular weights (by Dr. W. T. Chambers).—Number-average molecular weights, \bar{M}_n , were determined in benzene solution at 25° C using modified Zimm-Myerson osmometers and nitrocellulose membranes. The osmometers were designed for syringe filling and emptying, and had cell diameters of 20 mm. and capillary diameters of 0.5 mm. The membranes were approximately 2 mils thick and the "permeability constant"^{11,12}, P , to benzene in the range 6×10^{-6} to 8×10^{-6} . These membranes were of the lowest permeability for convenient usage and required ~ 24 hours for equilibrium. Membranes of double and triple the above P values registered pressures which were somewhat lower but no less stable giving for the original GR-S $\bar{M}_n = 217,000$

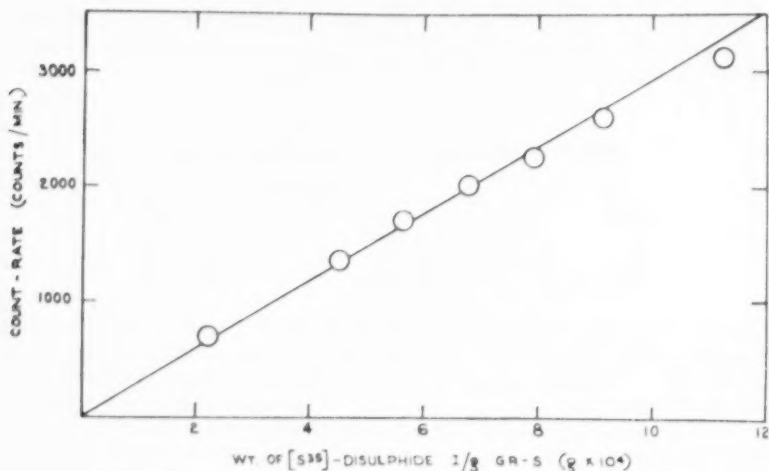


Fig. 8.—Calibration curve relating activity (counts/min.) of polymer film with weight of [S³⁵]-disulfide I per gram of GR-S (g. $\times 10^4$).

and $\mu = 0.382$. Some scatter in the observed pressures was obtained even when membranes were cut from the same film. For this reason all samples were measured in two osmometers and the results for each osmometer evaluated separately.

Instead of making single or duplicate pressure measurements at several approximately equally spaced concentrations as is customary, a linear regression for π/C with C has been assumed¹² and replicate measurements of π made at each of two concentrations (~ 1 per cent and $1/3$ per cent w/w). A replicate involves emptying and refilling with fresh solution, applying a positive head and observing the osmotic height after 1 day. Pressures were stable for at least three days. At each concentration at least four measurements were made in each osmometer. \bar{M}_n and μ (Table VI) have been calculated from the means of the observed pressures. To obtain an estimate of probable minimum and maximum values of \bar{M}_n , the probable limits of π have been taken as mean $\pi \pm 1/2$ (observed range of π). A maximum value for \bar{M}_n has been calculated from the lower limits of π at each concentration and a minimum value of \bar{M}_n

from the upper limits. In one instance (because of a ruptured membrane) \bar{M}_n was calculated from observations at the lower concentration only, using the mean of the observed μ values. The error involved is believed to be very small because of the excellent agreement between the independent estimates of μ .

EXPERIMENTAL RESULTS

Extraction of uncombined $[S^{35}]$ -disulfide from masticated GR-S.—GR-S was masticated with inactive disulfide under identical conditions to those used later for mastications in the presence of $[S^{35}]$ -disulfide. Most of the inactive disulfide was removed by acetone extraction and the masticated GR-S (3.259 g.) in benzene (100 ml.) was mixed with $[S^{35}]$ -disulfide I (0.1654 g.), the homo-

TABLE IV

Period of cold acetone extraction (days)	7	10	16
Activity of GR-S (counts/min.)	32	28	30

genized solution freeze-dried, and the dry active GR-S sample subjected to cold acetone extraction under nitrogen. The activity of the GR-S sample before extraction, when assayed under the standard conditions described above, would have been 1.5×10^6 counts/minute. The activities of the GR-S after different periods of extraction are given in Table IV. The results indicate the adequacy of the extraction method for the complete removal of uncombined $[S^{35}]$ -disulfide. For each assay, the vacuum-dried extracted sample was cold-masticated for 2 minutes, in air to destroy a small gel component formed in the extraction process. Such mastication is not expected to vitiate the quantitative determination of combined $[ArS^{35}]$ groups in the cold mastication experiments.

TABLE V

COLD ACETONE EXTRACTION OF COLD-MASTICATED GR-S:
 $[S^{35}]$ -DISULFIDE SAMPLES

Extraction period (days)	Activity of sample 1 (counts/min.)	Activity of sample 2 (counts/min.)
7	1415	—
10	1375	—
15	—	1515
16	1370	—
25	—	1450

Cold-mastication of GR-S with $[S^{35}]$ -disulfide.—A homogeneous solution of GR-S (3.916 g.) and $[S^{35}]$ -disulfide I (0.2108 g.) in benzene was freeze-dried and the dry polymer saturated with nitrogen during one hour. The sample was rapidly transferred to the small masticator⁵ and masticated for one hour at 30° C under nitrogen. The masticated sample (4.118 g., loss 0.01 g.) was re-dissolved in benzene under nitrogen to obtain a homogeneous polymer sample, and the solution freeze-dried. Part of the sample was used directly for the osmotic molecular weight measurements and the remainder cold-acetone extracted to constant activity (Sample 1, Table V).

An identical experiment to the above was conducted using a homogeneous mixture of $[S^{35}]$ -disulfide I (0.1847 g.) and GR-S (3.948 g.). The activities of the extracted GR-S (Sample 2) are given in Table V.

Conclusion.—The cold mastication of GR-S polymer in nitrogen in the presence of 1,1'-dinaphthyl $[S^{35}]$ -disulfide results in the incorporation of 1-naph-

TABLE VI
CORRELATION OF PHYSICAL AND RADIOCHEMICAL ESTIMATES OF COMBINED 1-NAPHTHYL [²⁴] GROUPS IN MASTICATED GR-S

Polymer sample	$\bar{M}_n (\times 10^{-3})$		$m = (1/\bar{M}_{n,0}) (\times 10^9)$		Activity calculated from m (counts/min.)		Observed activity (counts/min.)
	Osmometer 1	Osmometer 2	Osmometer 1	Osmometer 2	Osmometer 1	Osmometer 2	
Original GR-S							
Max. value ^a	1.89 ($\mu = 0.384$) ^b	1.83 ^c					
Min. value ^a	1.93	1.88					
Masticated GR-S, sample 1							
Max. value ^a	1.49 ($\mu = 0.382$)	1.41 ($\mu = 0.385$)	1.42	1.63	1345	1545	1370
Min. value ^a	1.55	1.47	1.76	2.03	1665	1925	—
Masticated GR-S, Sample 2							
Max. value ^a	1.44	1.36	1.05	1.19	1000	1125	—
Min. value ^a	1.55 ($\mu = 0.386$)	1.35 ($\mu = 0.394$)	1.16	1.94	1100	1840	1450
	1.62	1.39	1.53	2.26	1450	2140	—
	1.49	1.32	0.77	1.58	730	1495	—

^a Max. and min. values of \bar{M}_n are defined in the experimental section; max. and min. values of m are obtained using max. and min. values, respectively, of $\bar{M}_{n,0}$, together with the min. and max. values, respectively, of $\bar{M}_{n,0}$.

^b μ (polymer-solvent interaction coefficient) for GR-S and benzene at 25°. For this system at 30°, French and Ewart¹² found $\mu = 0.36$ and 0.37 for \bar{M}_n of 130,000 and 220,000, respectively.

^c Calculated from measurement at one concentration using mean value of $\mu = 0.386$.

thyl [S^{35}] groups into the degraded polymer (Table V). On the basis of the proposed mechanism, by which each polymer radical is terminated by a sulfenyl group, it follows from equation (1) that:

$$\text{moles of disulfide combined/g. polymer} = m \quad (3)$$

The correlation between the chemical and physical estimates of disulfide combined is given in Table VI, where it is shown that reasonable agreement is obtained between the calculated activity, based on the preferred values of $\bar{M}_{n,0}$ and $\bar{M}_{n,m}$, and the experimentally observed activity. The results clearly substantiate the mechanical degradation mechanism of polymer degradation for GR-S.

SYNOPSIS

The mechanism of cold mastication of natural and synthetic rubbers, as proposed by Kauzmann and Eyring, and by Pike and Watson, involves the mechanical rupture of the polymer chain yielding polymer radicals which are stabilized by interaction with radical-acceptor molecules to give the degraded polymer. This mechanism has been verified by a spectroscopic study of the cold mastication of natural rubber with 1,1-diphenyl-2-picryl hydrazyl and a radioisotopic tracer study of the cold mastication of GR-S using [S^{35}]-labeled 1,1'-dinaphthyl disulfide as the radical-acceptor molecule. Correlation of the decrease in molecular weight of the polymer and the amount of radical acceptor incorporated during the cold mastication process agrees with prediction according to the mechanical degradation mechanism.

ACKNOWLEDGMENTS

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MASTICATION OF RUBBER. IV. POLYMERIZATION OF VINYL MONOMERS BY THE COLD MASTICATION OF RUBBER *

D. J. ANGIER AND W. F. WATSON

THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
48 TEWIN ROAD, WELWYN GARDEN CITY, HERTS, ENGLAND

The softening of rubbers on cold mastication is a consequence of scission of the rubber molecules by the applied shear¹. Under the normal conditions of mastication in air, the free radicals at the ruptured ends of the polymer chains react predominantly with oxygen molecules. On masticating under oxygen-deficient conditions, usually in nitrogen, other reactions of the free radicals become significant and may yield rubbers with special chemical or physical properties. In particular, interpolymers are formed by the mastication together of two elastomers². Another general method of interpolymer formation is to utilize the radicals from chain rupture to initiate the polymerization of a monomer present in the rubber being masticated. Reported below is the application of this method with respect to a range of vinyl monomers in natural and synthetic rubbers.

EXPERIMENTAL MATERIALS AND METHODS

Elastomers.—Thinly sheeted deproteinized natural rubber² with N 0.09%, O 0.35%, ash 0.1%, $[\eta]$ 3.9 g.⁻¹ 100 ml., and gel < 1% was extracted for 16 hours by hot acetone in a Soxhlet apparatus to remove the 1.55 per cent of non-rubber constituents. After drying at 1 mm. Hg pressure overnight, the rubber was stored in vacuo.

Synthetic elastomers and monomers were obtained from commercial sources. Neoprene (grade WRT of Du Pont Ltd.) was extracted by methanol and dried, to give on analysis C 53.3%, H 5.65%, Cl 40.0%, ash 0.7%, and $[\eta]$ 1.08 g.⁻¹ 100 ml. It was also precipitated twice from benzene with methanol. Butadiene-styrene rubber (Polysar S-50) of styrene content 32.1%, $[\eta]$ 1.96 g.⁻¹ 100 ml., butadiene-acrylonitrile rubber (Krynac), Butyl rubber (Polysar 200), and polyisobutylene were similarly purified. Polyester-amide rubber (Vulcaprene A) was twice precipitated from acetone by methanol.

Monomers.—Methyl methacrylate and methyl and ethyl acrylates were washed with 10 per cent aqueous NaOH and distilled water, and dried over CaCl₂. Methacrylic and acrylic acids were rapidly distilled at 10⁻¹ mm. Hg and stored at -40° C. Styrene and acrylonitrile were distilled at ca. 20 mm. Hg pressure. Divinylbenzene (Dow Chemical Co.) supplied as a 50-60 per cent solution was distilled at ca. 20 mm. Hg pressure; the other component (ethylvinylbenzene) also polymerized under the reaction conditions. Chloroprene in xylene (Du Pont Ltd.) was washed with alkali and fractionated at atmospheric pressure immediately before use. The solid monomer, acrylamide (American Cyanamid Co.), was not further purified.

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Mastication of rubber containing monomer.—Measured volumes of monomer were dripped on to a fixed weight (3.00 ± 0.03 g.) of rubber, which was then allowed to stand for 16 hours in the dark to obtain homogeneous dispersion, except that only a 1 hour imbibition period was allowed for chloroprene owing to its ease of polymerization. The amount of monomer incorporated was determined gravimetrically just before insertion in the masticator.

The laboratory masticator used has been previously described². The chamber volume was varied to give suitable shear conditions depending on the amount of monomer added—the volumes were 4.9, 5.4, 5.9, 6.6, 7.3, and 7.9 ml. for 0, 0.5, 1, 2, 3, and 4 ml. of monomer in 3 g. rubber, respectively. The machine was flushed with nitrogen for 30 seconds and a positive pressure of nitrogen maintained during mastication. The lower scroll rotated at 76 r.p.m. The cooling water kept the polymerizing system to within a few degrees of 15° C before any rapid onset of polymerization; thereafter, inadequate dissipation of heat of reaction and increasing applied shear raised the temperature, maxima of ca. 50° C being measured for the extreme cases of methyl methacrylate, styrene, and acrylic acid in natural rubber at 90 per cent conversion. The mixture was finally sheeted on a 12 inch mill. Rubber not recovered after mastication was less than 0.2 per cent. Loss of monomer depended on volatil-

TABLE I
REPRODUCIBILITY OF POLYMERIZATION OF 37.7% STYRENE IN
NATURAL RUBBER BY MASTICATION

Series	Mastication, min.				
	20	40	60	80	100
a	10.9%	23.1%	48.9%	87.7%	97.2%
b	14.1	27.1	50.7	93.0	96.6

ity and time of reaction, usually being less than 3 per cent except for chloroprene, which gave losses of 6 and 9 per cent for 1 ml. and 3 ml. initially present, respectively.

Reproducibility of extent of polymerization varied with the shape of the extent-time curves. With small induction periods and relatively slow subsequent polymerization, reproducibility was within a few per cent throughout conversion, the small differences being due to variation of the induction period (e.g., styrene, Table I). With induction periods followed by rapid polymerization, reproducibility was within only ± 5 per cent over the brief time interval of rapid polymerization due to variation of shear conditions (e.g., methyl methacrylate, Figure 1). With low rates of polymerization, the rate was sensitive to small changes of conditions or traces of adventitious retarder (e.g., chloroprene, Figure 5).

Measurement of extent of polymerization.—To determine the extent of polymerization, the masticated mixture was weighed and then the unreacted monomer pumped off at 10^{-2} mm. Hg pressure over 24 hours. Control mixtures of monomer in rubber gave no measurable thermal polymerization during the period of mastication and evacuation. Gravimetric measurements of extent of polymerization were checked by determining plastomer present by elemental (including direct oxygen) or ultraviolet spectroscopic analysis.

Product analysis.—The amount of gel and its swelling and composition were measured after 7 days in benzene at 25° as described previously². Degree of swelling is given as weight of benzene in unit weight of polymer.

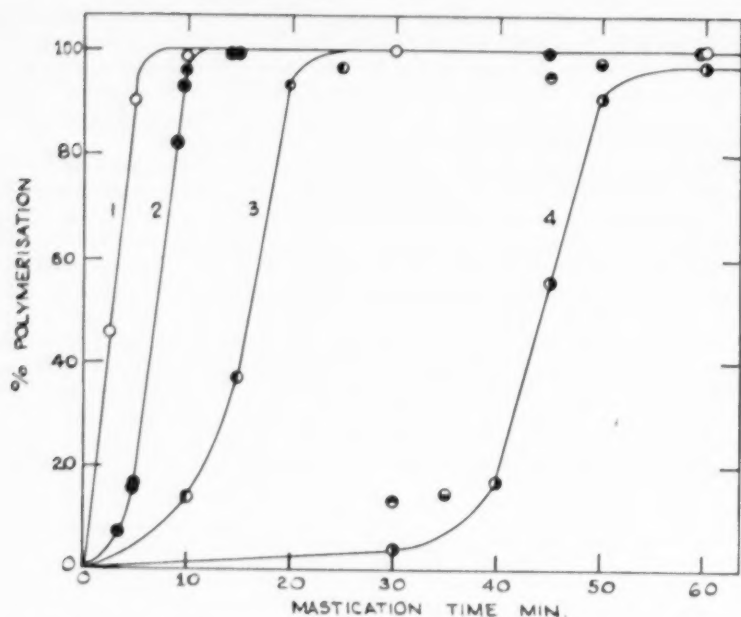


Fig. 1.—Effect of monomer concentration on polymerization of methyl methacrylate in masticating rubber. Initial monomer concentrations: (○) 23.8% methyl methacrylate; (●) 38.5% methyl methacrylate; (◐) 48.5% methyl methacrylate; (◑) 55.6% methyl methacrylate; (◒) 55.6% methyl methacrylate containing 1% benzoyl peroxide; (◓) 55.6% methyl methacrylate containing 1% bisazoisobutyronitrile.

The fractions of free (not interpolymerized) rubber and free polymethylmethacrylate in masticated mixtures were determined by selective solution with 60–80° C boiling petroleum ether and acetone, respectively. This separative method was accurate to 1–2 per cent for mixtures of the two polymers. Selective solution of the products after mastication gave reproducible soluble fractions after 4 days in solvents free from oxygen and similar values after 4–14 days under ordinary conditions (e.g., Table II). Solubility determination after 7 days without degassing was the standard procedure. Direct oxygen and infrared spectroscopic analysis confirmed that only the free polymers dissolved.

Free polystyrene was determined by heating the masticated mixture in a rubber mold at 140° C for 60 min. with 1.5 per cent di-*tert*-butyl peroxide, which insolubilized 94–96 per cent of the rubber. The free polystyrene was extracted by carbon tetrachloride, dried down, dissolved in chloroform, and its

TABLE II
SELECTIVE SOLUTION AFTER POLYMERIZATION OF 38.5% METHYL
METHACRYLATE IN NATURAL RUBBER

Solvent	% insoluble							
	Days in air				Days in vacuo			
	2	7	13	28	2	7	13	28
Petroleum ether	75.0	72.2	71.0	61.4	75.0	74.4	74.2	72.2
Acetone	87.2	83.1	78.7	Turbid	85.5	83.6	84.0	82.3

TABLE III
MONOMERS AS NONCROSSLINKING RADICAL ACCEPTORS IN
NATURAL RUBBER MASTICATION

Additive	Viscosity data					
	After 15 min.		30 min.		60 min. mastication	
	$[\eta]$	k'	$[\eta]$	k'	$[\eta]$	k'
None	2.19	0.54	1.82	0.53	1.67	0.58
Oxygen (air)	1.47	0.43	1.38	0.44	1.21	0.44
Benzoquinone, 1%	1.70	0.47	—	—	1.46	0.44
Chlorobenzene, 5%	2.52	0.50	—	—	—	—
Dibutyl phthalate, 5%	—	—	2.04	0.56	—	—
Methyl methacrylate, 5%	1.74	0.46	1.60	0.45	1.37	0.46
1%	1.95	0.46	1.70	0.47	1.43	0.46
Styrene, 1%	2.11	0.48	—	—	1.55	0.49
Vinyl acetate, 5%	2.15	0.53	1.84	0.47	1.59	0.49

concentration determined from the optical densities at 2620 and 2690 Å. Extinction coefficients⁴ obtained at these wave lengths for purified polystyrene were 2.22 and 1.63 g.⁻¹ l. cm.⁻¹. Synthetic mixtures analyzed correctly for polystyrene, e.g., for a 20 per cent mixture, 17 per cent after 3 days, 21 per cent after 7 to 14 days.

Bulk viscosity of the masticated mixture was measured by a Wallace Rapid Plastimeter and quoted as W.P. units of sample thickness after a 15 second period at 100° C under a compression of 12.7 kg./cm.² compared with an initial thickness⁴ of 100 units.

RESULTS

Monomers as radical acceptors.—Monomers must function as radical acceptors to be polymerized by masticating rubber. Radical-acceptor reactivity was tested by masticating under nitrogen rubber containing only small quantities of monomers (i.e., insufficient to cause viscosity changes due to the polymers formed) and measuring either the reduction in intrinsic viscosity or gel production¹. The monomers were classified as noncrosslinking or crosslinking acceptors depending upon whether they gave rubbers with Huggins' viscosity constants, k' , similar to those obtained on milling rubber with radical acceptors such as oxygen and thiophenol or gave gels, respectively². Methyl methacrylate and styrene were found to be noncrosslinking acceptors, chloroprene, acrylonitrile, and methacrylic acid to be crosslinking, and vinyl acetate to be as

TABLE IV
MONOMERS AS CROSSLINKING RADICAL ACCEPTORS
IN NATURAL RUBBER MASTICATION

Additive	Mastication conditions	Gel	
		%	Swelling
Chloroprene, 1%	15 min. in N ₂	45	20
	30 min. in N ₂	43	20
	15 min. in air	20	54
Acrylonitrile, 1%	5 min. in N ₂	66	12
	15 min. in N ₂	80	7
	15 min. in air	63	10
Methacrylic acid, 1%	5 min. in N ₂	34	34
	15 min. in N ₂	43	27
	15 min. in air	30	37

unreactive as the inert solvents, chlorobenzene and dibutyl phthalate (Tables III and IV).

Soluble interpolymers of natural rubber with methyl methacrylate and styrene.—The polymerization of these two monomers during mastication proceeded similarly, with styrene polymerizing somewhat more slowly. The products were soluble up to complete polymerization, in contrast with the products of the other monomers reported below.

The dependence of rate of polymerization on monomer concentration is shown in Figures 1 and 2. The most critical factors was the shear imposed, and therefore the rate of polymerization could be at least approximately corre-

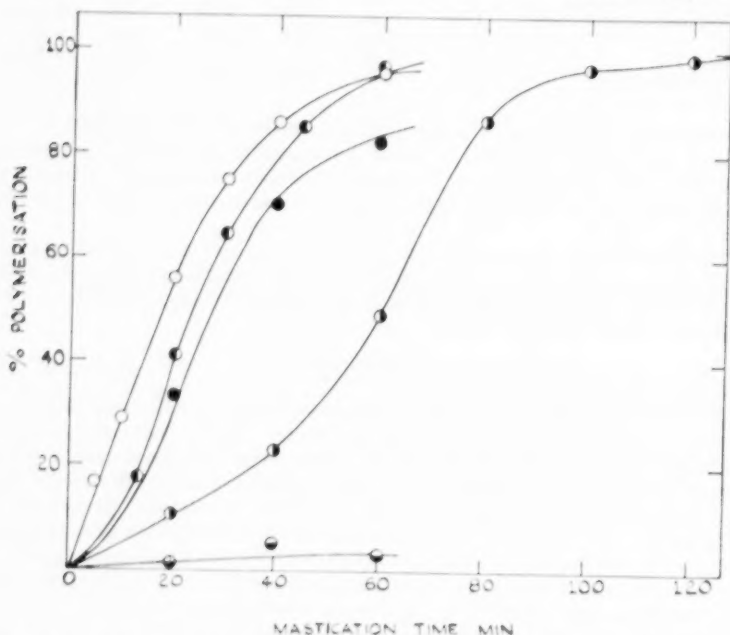


Fig. 2.—Effect of monomer concentration and temperature on polymerization of styrene in masticating rubber: (○) 13.2% styrene, 15° C; (●) 23.3% styrene, 25° C; (◐) 23.3% styrene, 15° C; (◑) 37.7% styrene, 15° C; (◒) 37.7% styrene, 25° C.

lated with the bulk viscosity of the mixture undergoing mastication. Increasing the amount of monomer served mainly to retard the early stages of polymerization. Small additions of monomer had little influence on the bulk viscosity and the relative rate of polymerization on mastication, but higher concentrations produced disproportionately marked plasticization and correspondingly long induction periods on mastication. The mixture remained soft and transparent during the induction period. Translucency and stiffening developed just before rapid polymerization and progressed to opacity and a hardness considerably greater than that of the original rubber (Tables V and VII). Hardness reached a maximum at between 90 and 100 per cent polymerization. Bulk viscosity, free rubber, and free polymethyl methacrylate data are reported in Table V.

TABLE V
FREE RUBBER AND FREE POLYMETHYL METHACRYLATE CONTENTS
AND BULK VISCOSITIES AFTER MASTICATION

System reference	Mastication time, min.	Polymerization, %	Viscosity W.P. units	% free rubber	% free plastomer
				Total rubber	Total plastomer
Figure 1, curve 1	2.5	46.0	61	69	11
	5	90.3	85	48	13
	10	98.7	68	43	10
	30	99.8	31	49	9
	60	100	30	61	12
Figure 1, curve 2	2	17.2	43	81	14
	10	96.2	94	39	13
	15	99.4	95	36	25
	45	99.8	56	44	47
	90	100	52	45	52
Figure 1, curve 3	10	14.0	39	79	24
	20	93.2	84	50	19
	25	97.0	95	48	27
	60	100	91	38	32
	40	17.9	38	77	15
Figure 1, curve 4	45	55.7	72	74	25
	50	91.2	98	60	12
	60	96.7	100	46	26

Benzoyl peroxide and azoisobutyronitrile did not increase the rate of polymerization except during the induction period, to be accounted for by crosslinking-acceptor reactivity rather than by radical-initiator reactivity¹.

Owing to their similar solubilities, free rubber and free polystyrene could not be determined by direct selective solution. Instead, one or other of these components was bound almost completely into a network and the extractable portion of the second taken as the fraction not interpolymerized. The rubber was crosslinked by di-*tert*-butyl peroxide (Experimental Section) while the styrene was crosslinked during polymerization by divinyl benzene (DVB); thus, 0.25 per cent DVB produced a gel containing all the polymerized monomer, from which a reproducible fraction of rubber was extractable (Table VI).

The effects of varying the shear conditions by changes of temperature and of rotor speed and by addition of inert solvent are illustrated in Figures 3 and 4.

TABLE VI
POLYMERIZATION OF 37.7% STYRENE WITH AND WITHOUT 0.25% DVB
IN NATURAL RUBBER ON MASTICATION

Mastication time, min.	% polymerization		Rubber crosslinking		Polystyrene crosslinking	
			% polystyrene in sol		% rubber in sol	
	without DVB	with DVB	% gel	Total polystyrene	% gel	Total rubber
20	12.5	9.5	91.5	30.3	20.8	85.2
40	25.1	24.0	91.3	24.8	36.3	72.9
60	49.8	46.8	91.0	16.9	44.3	71.4
80	90.4	92.9	91.8	12.8	63.6	56.8
100	96.9	93.7	93.0	12.4	65.1	47.2
120	98.1	99.7	92.6	12.3	62.4	48.8

The reaction possessed the unusual negative temperature coefficient associated with mechanical shear¹. Increase in rotor speed increased the initial rate of polymerization, but the potentially greater shear was not effectively realized (Table VII) because of thermal softening of the rubber by frictional heat and heat of reaction, e.g., temperature maxima of 32 and 52° C were obtained at 76 and 360 r.p.m., respectively. Dilution by benzene or carbon tetrachloride produced primarily an increase in induction period with total liquid concentration, and a less marked reduction in the later polymerization rate.

Insoluble interpolymers of rubber and monomers.—The rate of polymerization of chloroprene on mastication with natural rubber did not increase rapidly with conversion (Figure 5), as with methyl methacrylate and styrene. This difference in rate can be attributed to differences in the physical properties of the

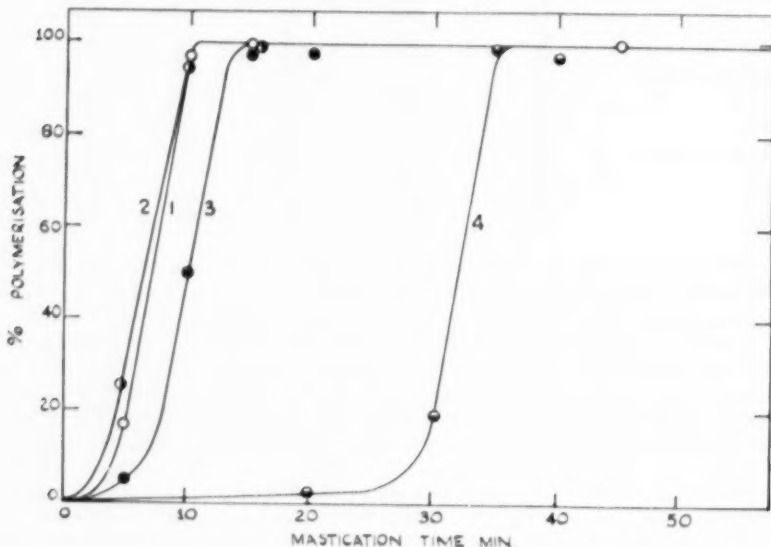


Fig. 3.—Effect of temperature on polymerization of methyl methacrylate in masticating rubber: (○) 38.5% methyl methacrylate, 15° C, 76 r.p.m.; (●) 38.5% methyl methacrylate, 15° C, 360 r.p.m.; (○) 38.5% methyl methacrylate, 25° C, 76 r.p.m.; (●) 38.5% methyl methacrylate, 35° C, 76 r.p.m.

polymerized materials; the chloroprene-rubber system remained elastic and softer than the original rubber (as expected from the properties of polychloroprene). The product was partly insoluble in benzene and the proportion of insoluble gel, which contained most of the polychloroprene, increased with time of mastication (Table VIII).

Acrylic acid, methacrylic acid, methyl and ethyl acrylate, acrylonitrile, acrylamide, and divinylbenzene all polymerized rapidly and completely on masticating with natural rubber under nitrogen unless the physical condition of the modified rubber prevented the continued application of shear. Gel fractions were produced containing all the polymerized monomer and a large proportion of the rubber (Table IX).

In all cases, the physical properties of the masticated mixture differed greatly from those of the original rubber. Divinylbenzene gave a tough coherent

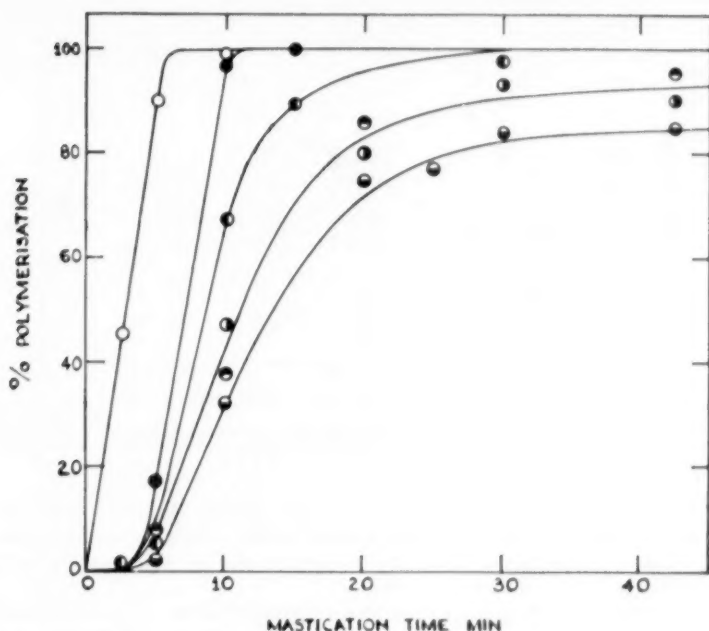


Fig. 4.—Effect of solvents on polymerization of methyl methacrylate in masticating rubber: (○) 23.8% methyl methacrylate; (●) 38.5% methyl methacrylate. Vol. 2 ml. of concentrations: (○) 2:1 methyl methacrylate: C_6H_6 ; (●) 1:1 methyl methacrylate: C_6H_6 ; (●) 1:1 methyl methacrylate: CCl_4 ; (●) 1:2 methyl methacrylate: C_6H_6 .

interpolymer, comparable with that obtained with styrene. Acrylic acid gave at an initial 25 per cent concentration a hard rubber, and at 40 per cent initial concentration an unyielding material that stopped the masticator. The acrylates and acrylonitrile produced a rubber "crumb" similar in appearance to the

TABLE VII
FREE RUBBER AND FREE POLYMETHYL METHACRYLATE CONTENTS
AND BULK VISCOSITIES AFTER MASTICATION

System reference	Mastication time, min.	Polymerization, %	Viscosity, W.P. units	% free	
				rubber Total rubber	plastomer Total plastomer
Figure 3, curve 2	5	27.2	23	85	0
	10	92.8	35	69	10
	15	98.4	52	52	36
	90	100	48	61	51
Figure 3, curve 3	10	49.2	39	81	3
	15	97.0	76	49	25
	20	97.1	72	49	24
	90	90.0	58	59	36
Figure 3, curve 4	30	19.6	32	94	0
	35	98.7	71	45	7
	40	96.8	62	53	15
	90	100	48	50	21

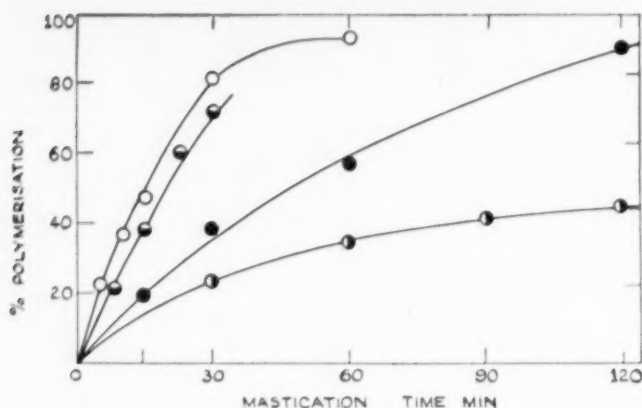


Fig. 5.—Effect of monomer concentration and temperature on the polymerization of chloroprene in masticating rubber: (O) 24.2% chloroprene, 15° C; (●) 39.0% chloroprene, 15° C; (◐) 24.2% chloroprene, 25° C; (◑) 49.0% chloroprene, 15° C.

product given by maleic anhydride⁶. Samples containing more than 40 per cent acrylamide gave, after 2 hours milling, a fine powder resembling talc in appearance with negligible solubility in benzene and no coherence on heating with sulfur at 140° C under pressure.

Two monomers.—Polymerization of a constant volume of 2 ml. of methyl methacrylate-styrene mixtures in 3 g. rubber gave polymerization-time curves of the same general shape as, and intermediate between, those of the two separate monomers (Figure 6). The composition of the polymers produced are given in Figure 7.

Polymerization of methyl methacrylate-chloroprene showed a markedly different behavior. Chloroprene had to be used immediately after alkali washing and distillation as a few hours' standing in air at room temperature or over-

TABLE VIII
POLYMERIZATION OF CHLOROPRENE BY NATURAL RUBBER MASTICATION

Initial monomer concn., %	Mastication time, min.	Polymerization, %	%	Swelling	Gel	
					% elastomer in gel	% rubber in gel
23.9	5	22.8	39.3	26	67	37
	10	36.1	43.5	22	72	40
	15	47.2	47.4	18	78	43
	30	81.7	61.8	11	85	56
	60	93.3	67.3	10	89	61
38.4	15	19.3	26.2	47	71	21
	30	38.3	28.7	30	74	18
	60	57.3	38.2	19	73	26
	120	89.8	57.0	9	83	42
49.0	30	24.2	49.8	20	91	41
	60	35.4	59.0	15	85	51
	90	42.4	62.9	11	93	52
	120	46.6	62.7	10	88	54

TABLE IX
POLYMERIZATION OF MONOMERS BY NATURAL RUBBER MASTICATION

Monomer	Concn., g./100 g. rubber	Masti- cation time, min.	Polymer- ization, %	%	Swell- ing	Gel	
						% plastomer in gel	% rubber in gel
						Total plastomer	Total rubber
Acrylic acid	35	2.5	100	79	4	100	72
	35	10	100	79	5	100	72
Methacrylic acid	34	1	12	29	21	100	27
	34	1.75	57	56	6	100	48
	34	3.5	100	78	4	100	71
	34	7.5	100	77	5	100	70
Methyl acrylate	31	10	62	86	10	100	82
Ethyl acrylate	32	10	42	91	10	100	90
Divinylbenzene soln.	23	5	18	70	15	100	69
	23	7.5	30	76	9	100	73
	23	10	51	79	7	100	76
	23	15	87	84	3	100	79
	23	20	99	87	4	100	86
	23	30	98	88	4	100	85

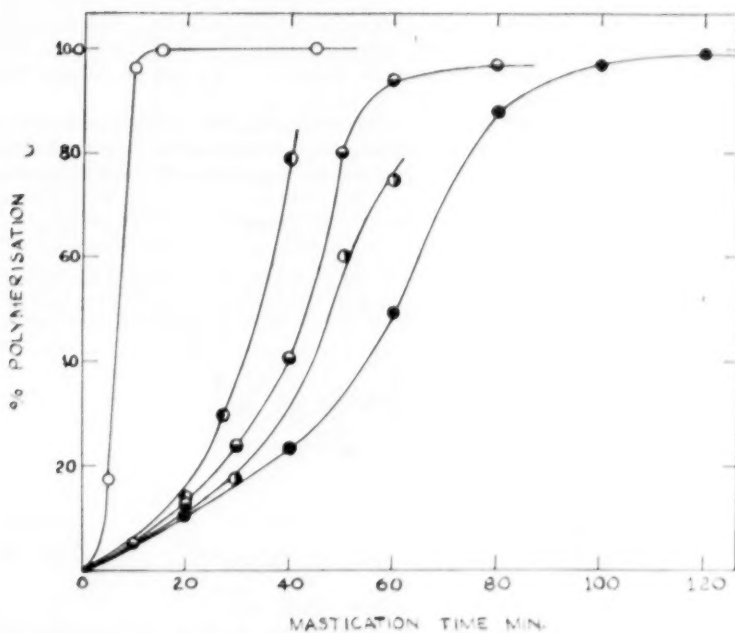


FIG. 6.—Copolymerization of methyl methacrylate and styrene in masticating rubber: (○) 38.5% methyl methacrylate; (●) 37.7% styrene; (◐) 25.7% methyl methacrylate and 12.6% styrene; (◑) 19.3% methyl methacrylate and 18.9% styrene; (◒) 12.8% methyl methacrylate and 25.1% styrene.

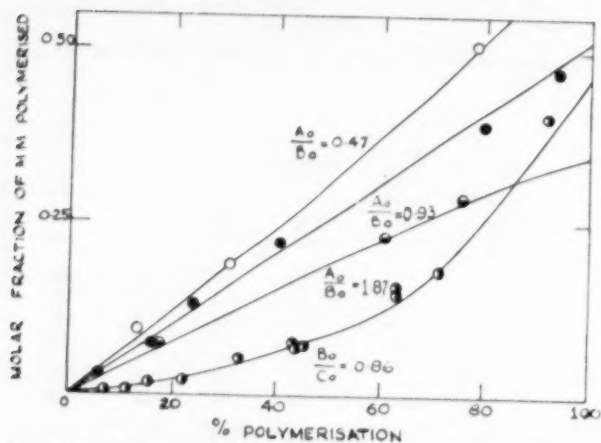


Fig. 7.—Composition of copolymers formed by rubber mastication: (A_0 , B_0 , C_0) initial molar fractions of styrene, methyl methacrylate, and chloroprene, respectively. (Full lines) calculated compositions based on r_1 and r_2 values of 0.50 and 0.44 for styrene and methyl methacrylate⁸ and of 0.083 and 6.12 for methyl methacrylate and chloroprene⁹.

night at -40°C allowed the formation of a volatile impurity that did not influence the rate of chloroprene polymerization but greatly retarded that of methyl methacrylate. The rate of polymerization was initially slower than that of the slower monomer (chloroprene) and passed through a reproducible minimum slightly below 50 per cent polymerization (Figure 8, curve 1). The composition of the copolymer is given in Figure 7. (No loss of chlorine from the copolymer was found on storage⁷ for 13 days at -40°C .)

Synthetic rubbers.—As commercially available, the synthetic rubbers—neoprene, polybutadiene-styrene, polybutadiene-acrylonitrile, polyisobutylene, and ester-amide rubber—did not polymerize monomers on mastication but

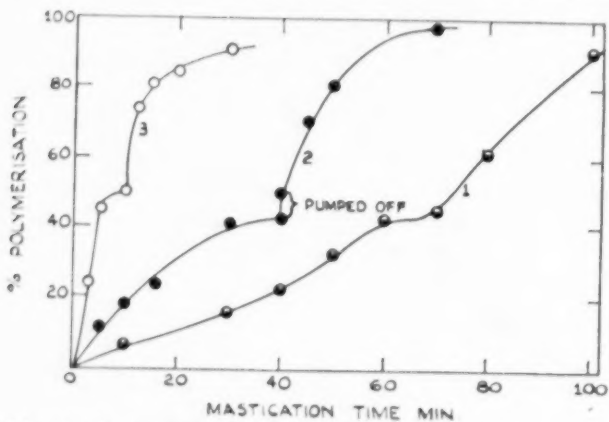


Fig. 8.—Polymerization of methyl methacrylate and chloroprene by rubber mastication: (○) Curve 1, 23.8% methyl methacrylate and 24.2% chloroprene added initially; (●) Curve 2, 24.2% chloroprene polymerized, then 23.8% methyl methacrylate; (○) Curve 3, 23.8% methyl methacrylate polymerized, then 24.2% chloroprene.

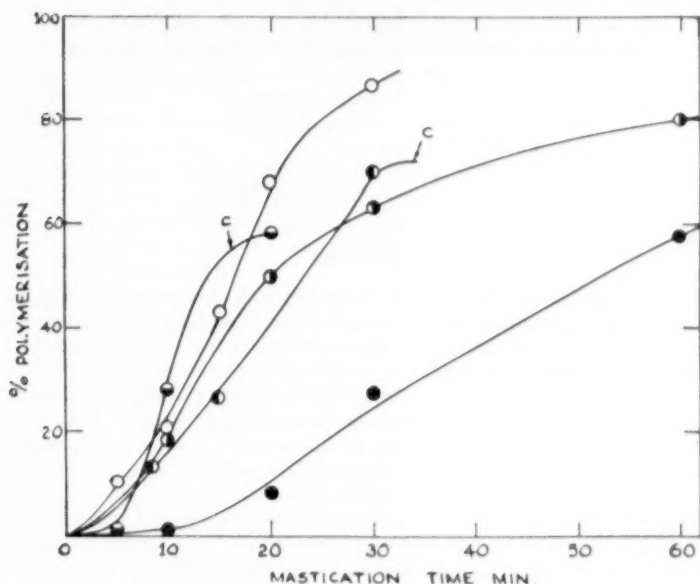


FIG. 9.—Polymerization initiated by the mastication of synthetic rubbers: (O) 13.8% methyl methacrylate in neoprene; (●) 13.6% chloroprene in neoprene; (◐) 13.8% methyl methacrylate in polybutadiene-styrene; (◑) 13.6% chloroprene in polybutadiene-styrene; (◒) 14.5% styrene in polybutadiene-acrylonitrile. "c" indicates that the rubber became a crumb at approximately the arrowed time of mastication.

merely underwent degradation. However, after two precipitations to remove antioxidant, and a lower molecular fraction, polymerization readily occurred on mastication (Figure 9 and Table X). Butadiene-acrylonitrile rubber crumbed with all the monomers tested, viz. methyl methacrylate, styrene, methacrylic acid, and acrylonitrile.

Since polyisobutylene and polyester-amide rubbers had not been previously tested for the production of polymeric radicals on cold mastication by the action of typical radical acceptors¹, their degradation on masticating under nitrogen after the addition of thiophenol was investigated (Table XI).

TABLE X
POLYMERIZATION OF MONOMERS ON MASTICATING
WITH SYNTHETIC RUBBERS

Elastomer	Monomer	Initial % monomer	Masti- cation time, min.	% polymer- ization
Butyl rubber	Methyl methacrylate	11.9	30	8.5
		11.9	60	91.8
	Styrene	11.6	30	0
			60	5.7
Polyisobutylene	Methyl methacrylate	11.9	30	76.5
Vulcaprene	Methyl methacrylate	23.8	30	87.5
	Styrene	23.2	30	75.5

TABLE XI
DEGRADATION OF SYNTHETIC RUBBERS ON COLD MASTICATION

Rubber	Initial intrinsic viscosity	Intrinsic viscosity on mastication in air	Intrinsic viscosity on mastication in N ₂ with 1% thiophenol
Butyl rubber	0.40	0.35 (30 min.)	0.34 (30 min.)
Polyisobutylene	0.66	0.60 (30 min.)	0.49 (30 min.)
Vulcaprene	0.67	0.56 (60 min.)	0.55 (60 min.)

DISCUSSION

The rapid polymerization at low temperatures, the negative temperature coefficient, and the conditions of reaction are evidence for initiation by the free radicals produced by rupture of rubber molecules by the applied shear. Both chemical and physical properties of the rubber influence the reaction. The more reactive rubbers possess in their chemical structure certain bonds at which rupture is facilitated by unsaturation in the backbone chain¹. However, this structural limitation is not rigorously exclusive since the essentially saturated chains of polyisobutylene and ester-amide rubbers also initiate polymerization. To be efficient initiators, rubbers must also be of sufficiently high bulk viscosity and molecular weight for imposition of shear and consequent scission. These same factors influence the degradation of the rubber by the normal cold mastication process and therefore an approximate correspondence exists between softening on mastication in air and initiation of polymerization under nitrogen. In this connection, natural rubber is plasticized by cold mastication more readily than the common synthetic rubbers, and so this property, which may be a disadvantage in control of normal processing, appears as an advantage in promoting reaction with polymerizable substances.

Polymerization also depends intimately on the chemical and physical properties of the monomer. Concerning chemical properties, the monomer must be sufficiently reactive for initiation of polymerization by the radical from the rubber; the failure of vinyl acetate to polymerize during mastication can be attributed to the low reactivity of allyl radicals toward this monomer⁶. Gelation occurs on mastication with dienes and other monomers that also give gels on thermal polymerization. Concerning physical properties, a high compatibility of rubber and monomer leads to slower reaction due merely to the resultant softening reducing initiation by shear. The influence of solvents can be similarly ascribed, dilution of monomer being a secondary factor. It is probable that the viscosity influences the polymerization as at later stages of bulk polymerization⁷, but this is difficult to ascertain without structural analysis of the products (to be reported elsewhere) owing to the complexity of the over-all reaction.

The physical properties of the polymer formed are also important. With hard plastomers, their formation appears to be the most important factor controlling the rate of polymerization after the initial stages. Conversely, the relatively slow polymerization of the very reactive monomer, chloroprene, is attributable to the soft and elastic nature of its polymer.

With two monomers, different rates of polymerization and different products are observed, depending on the method of monomer addition. For the two monomers added initially, the composition of the polymer is controlled by the monomer reactivity ratios. With the approximately equal reactivity ratios in

the system methyl methacrylate-styrene¹⁰, the composition of the plastomer formed was approximately that of the initial monomer mixture added to the rubber. Rates of copolymerization were intermediate between those of the separate monomers. With the large difference in monomer reactivity ratios in the chloroprene-methyl methacrylate system⁷, the two monomers largely polymerized separately. Initial rates were low because of the soft polychloroprene formed and the solvent effect of the methyl methacrylate, and only increased on production of appreciable amounts of polymethyl methacrylate after almost all the chloroprene had been consumed. Two-stage polymerization of the two monomers occurred more rapidly, especially if methyl methacrylate was polymerized first.

A technological evaluation of interpolymers formed by cold mastication is in progress. Preliminary results show: (1) polymerization can be initiated by common grades of natural rubber without purification; (2) by suitable design of masticator, adequate oxygen-deficient conditions for polymerization can be realized without the use of nitrogen; and (3) the elastic and solvent properties of the vulcanizates produced are markedly influenced by the plastomer component.

SUMMARY

The rupture of natural and synthetic rubber molecules into free radicals by the shear imposed during cold mastication under nitrogen initiates the polymerization of monomers incorporated in the rubber. Experimental results on the polymerization of a range of monomers is reported. The polymer formed is mainly attached to the rubber, forming with it either a soluble interpolymer or a two-component gel depending on the monomer used. Results on the copolymerization of two monomers are also presented and interpreted.

ACKNOWLEDGMENT

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CROSSLINKING OF LATEX RUBBER *

E. M. BEVILACQUA

UNITED STATES RUBBER COMPANY, PASSAIC, NEW JERSEY

Most of the properties of rubber are consistent with those expected of a high-molecular-weight linear polymer of isoprene. However, there are some features of its behavior that are inexplicable on this basis. They must be the result of the presence of small amounts of structures other than the regular head-to-tail chain of isoprene units.

Bloomfield, in the first fundamental study¹ of the properties of rubber from freshly tapped latex, found that the tree does not continue to build indefinitely a linear polymer, but that branching reactions occur in a rested tree. These reactions eventually convert individual latex particles into substantially single molecules of enormous molecular weight. Bloomfield also observed that small amounts of oxygen are intimately associated with the hydrocarbon, even when it is isolated directly from the tree with careful exclusion of atmospheric oxygen. Craig, Juve, and Davidson² have found less certain indications of the presence of carboxyl groups, which, if they are present in the rubber in concentrations even approaching the amount indicated by their results, must be on side chains.

Watson³ discovered evidence for unique links in the hydrocarbon chain at intervals of about 700,000 in molecular weight; these links dissociate at a measurable rate in solution. He has suggested that these links may be responsible for the slow "gelation" of massive rubber. Messenger⁴ showed that this reaction is inhibited by water; samples stored in the presence of desiccants progressively increased in molecular weight (actually in solution viscosity) and finally became increasingly insoluble in the usual rubber solvents. This has recently been substantiated by further work by Wood⁵ in connection with the "Technically Classified" rubber⁶ program.

A less well known phenomenon, although it is familiar to users of commercial latex, is the rapid development of high viscosity and relative insolubility in rubber that is obtained from preserved latex. Such rubber may become as high as 80-per cent insoluble in benzene and have "Mooney" viscosities⁷ of more than 100.

During the period 1948-50, the Plantations Division of the United States Rubber Company imported a number of samples of latex that had been preserved in a variety of ways, in the course of an intensive study of preservation methods. As a result, it was possible to obtain data which indicate that the preservative⁸ used has a specific effect on the viscosity of the rubber (Table 1). Among other tests on the latexes, the solubility in benzene and the Mooney viscosity (ML4-212) of the rubber obtained by drying samples of the latex at room temperature were measured. Solubility was determined by the conventional procedure (developed for GR-S) in which 0.5 g. of rubber supported on steel screens is left in contact with 75 ml. of solvent for 24 hours in the dark, after which the concentration of an aliquot of the solution is determined.

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TABLE 1
EFFECT OF PRESERVATIVE ON GEL AND VISCOSITY.

Latex No.	pH	Ammonia*	Other amines†	Gel (%)	MLA-212
63	11.3	—	—	0	99
47	10.4	+	—	59	118
48	10.4	+	—	38	111
66	10.4	+	—	60	>110
68	10.4	—	+	30	98
72	10.3	+	—	65	>110
73	10.3	+	—	49	103
57	10.3	+	—	52	108
35	10.3	+	—	58	111
40	10.2	—	+	16	87
74	9.8	+	—	39	>110
157	9.7	—	+	12	67
58	9.6	—	+	12	64
37	9.4	—	+	18	71
38	9.4	—	+	7	64
64	9.4	—	+	12	63
62	9.3	—	+	12	72
67	9.2	—	+	9	79
60	9.1	—	+	13	84
75	8.9	—	+	9	76
27	8.7	—	+	29	70
23	8.3	—	+	8	65
61	8.3	—	+	12	76
24	7.2	—	+	17	
39	6.9	—	+	15	77
12	6.6	—	+	15	84
1	5.8	—	—	18	75

* —, preservative absent; +, present.

† Amines other than ammonia were all low-molecular-weight aliphatic amines. Dimethylamine was the sole preservative in latex 68.

There were not available enough high pH latexes containing no ammonia to eliminate entirely pH as a factor, but only those latexes containing free ammonia have the combination of Mooney viscosity greater than 100 and percentage gel greater than 30, indicating strongly that ammonia has a specific effect of increasing the extent of crosslinking in the latex rubber.

This is a positive effect—that is, it does not result from inhibition of degradation by oxygen during storage and handling of the latex. The rate of reaction of oxygen with latex is highest in the range of pH of commercial latex⁹, and it falls sharply when the pH is less than 9. The rubber from fresh latex from trees tapped regularly is usually soluble, and its Mooney viscosity is in the range of 60 to 80. Further, the viscosity increase can be induced in latexes that have been preserved without ammonia.

TABLE 2
EFFECT OF AMMONIA ON LOW pH LATEXES

Latex	MLA-212 after 6 months	
	Control	Ammonia added
24	90	105
39	85	114
40	87	107
60	78	108
62	78	102

Small amounts of several of the low pH latexes listed in Table 1 were treated with ammonia (2 per cent) and left standing for 6 months. The rubber in all these samples increased markedly in viscosity as compared with controls (Table 2).

It appears quite possible that the same functional groups are responsible for the crosslinking induced by ammonia and that which occurs during storage of dry rubber. During the development of the USF rubber process C. E. Linscott¹⁰ observed that brief treatment with ammonia of the latex or of freshly precipitated rubber from formaldehyde-preserved latex caused an immediate rise of Mooney viscosity and accelerated the later slow rise of viscosity during storage of the dry rubber.

The fragility of the swollen gel makes it difficult to determine precisely the volume ratio of solvent to rubber. Molecular weights between crosslinks¹¹ estimated from the figures available range from $\sim 5 \times 10^5$ for the samples with higher gel contents to more than 10^6 for the very tenuous gels frequently obtained from samples with low gel. The maximum observed extent of crosslinking is thus in reasonable accord with Watson's estimate of the concentration of unique linkages in rubber.

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CHARACTERIZATION OF GRAFT POLYMERS *

JOSEPH A. BLANCHETTE AND LAWRENCE E. NIELSEN

RESEARCH DEPARTMENT, PLASTICS DIVISION, MONSANTO CHEMICAL COMPANY,
SPRINGFIELD 2, MASSACHUSETTS

INTRODUCTION

Since the earliest recorded attempts to modify rubber by the polymerization of monomers dissolved in rubber¹ considerable work has been directed toward the preparation and characterization of copolymers other than those with random distribution based on the reactivity ratios of the two components. Block polymers consisting of A and B chains coupled to form a linear molecule have been reported by many investigators including Melville and coworkers² and Woodward and Smets³. Woodward and Smets⁴ used the different solubilities in selected solvents and their mixtures to separate block copolymers of styrene-methyl methacrylate and vinyl acetate-styrene from the two homopolymers with which they occurred. Solution properties of the isolated materials were then investigated.

This technique for isolation and characterization has been used with graft polymers in which branches containing all A are attached to a "backbone" of B units. Claesen and Smets⁵ prepared and separated vinyl acetate-polymethyl methacrylate and vinyl chloride-polymethyl methacrylate graft polymers from the homopolymer mixture by solubility differences and reported on the osmotic and viscometric behavior of the graft materials. Other investigators⁶ have studied conditions and techniques for preparing graft copolymers while attempting partial characterization of the materials produced by using solubility differences for isolation and the usual methods for property studies.

Recently⁷, graft polymers of rubber with styrene and methyl methacrylate have been prepared and fractionated into rubber, rubber-vinyl polymer compound, and free vinyl polymer. The relative amounts and the molecular weights of the three fractions were used to calculate the molecular weights of the attached side chains. This work provides the first clear-cut evidence of the combination between rubber and the vinyl polymer by graft polymerization as well as preliminary structural characterization in terms of attached vinyl polymer chains.

The present work is primarily concerned with the complete structural elucidation of styrene-rubber graft polymers by the modification and correlation of known techniques. The polymers were prepared by mass polymerizing rubber in styrene monomer and the graft copolymer isolated by careful fractionation of the mixture. The graft-copolymer fractions were analyzed for their butadiene-styrene content by an infrared technique and by a titration technique based on the use of perbenzoic acid⁸. The polystyrene chains were then removed from the rubber backbone by chemical cleavage and characterized separately. From these data the length and number of styrene chains were calculated so that a theoretical picture of the graft molecule could be postulated. The possibility now exists for correlating structure and properties and for ex-

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tending the technique to related materials. The preparation, analysis, and physical and mechanical properties of two graft polymers are here reported.

EXPERIMENTAL

PREPARATION OF STYRENE-RUBBER GRAFT POLYMERS

The materials were prepared by dissolving a GR-S rubber in styrene monomer and then mass polymerizing the solution using a peroxide catalyst. The polymerization was carried out at the reflux temperature in a flask equipped with a condenser, mechanical stirrer, and nitrogen inlet tube until the viscosity permitted pouring (approximately 8 hours). The materials were then transferred to wide-mouth jars which were flushed with nitrogen, sealed, and placed in an oil bath at 95° C. The temperature was gradually increased to 180° C as the polymerization progressed. Two materials prepared by this technique were designated as A and B. When the polymerization was essentially complete, the temperature of the material designated as B was raised to approximately 300° C for 10 minutes. Material A originally contained 10 per cent of a substantially gel-free GR-S rubber, while material B contained 6 per cent of this rubber.

FRACTIONATION OF A AND B

Since these materials are heterogeneous mixtures of rubber, polystyrene, soluble branched styrene-rubber, and insoluble styrene-rubber gel, the insoluble graft portions were isolated by solvent-nonsolvent fractionation. The fractionation technique here described was designed to resolve the materials into the component parts and compare the A and B polymers.

Ten grams of each polymer was dissolved in a mixture of 200 ml. of benzene and 150 ml. of methylethyl ketone. The undissolved gel was centrifuged out. The fractionations were then carried out by adding measured amounts of methanol, allowing the solutions to stand, and centrifuging off the insoluble portions. The gel was extracted until no further material could be removed and a totally insoluble fraction remained. Samples of polystyrene and GR-S rubber were also fractionated by the same technique. As additional proof that this technique is applicable, a mixture of GR-S rubber and polystyrene was subjected to the same treatment and was readily separated back into the pure components originally making up the mixture.

The results of the fractionations are shown in Figure 1. The weights of the A and B gel fractions were 2.231 and 1.306 g., respectively, at 0 ml. of methanol and the next fractions, A-1 (0.547 g.) and B-1 (0.125 g.), were obtained at 50 ml. of methanol. Seven fractions were isolated for each material.

Only the A and B gel structures were elucidated and are reported here since most of the other fractions were mixtures or polystyrene (although the first fractions were fairly pure soluble branched materials such as A_{1f1}) (see Figures 4 and 5).

DETERMINATION OF UNSATURATION (PERBENZOIC ACID)

Peracids such as performic, peracetic, and perbenzoic selectively oxidize olefinic type bonds to epoxides and glycols and have been found to be suitable reagents for the quantitative determination of vinyl unsaturation. The material under consideration is allowed to react with an excess of the peracid

according to the following equation:



The excess or unreacted peracid is treated with potassium iodide and the liberated iodine is titrated with a standard thiosulfate solution. A simple calculation gives the amount of peracid which reacted with an equimolar amount of olefinic unsaturation. Perbenzoic acid was chosen for this work because it is relatively stable and more readily adapted to quantitative analysis.

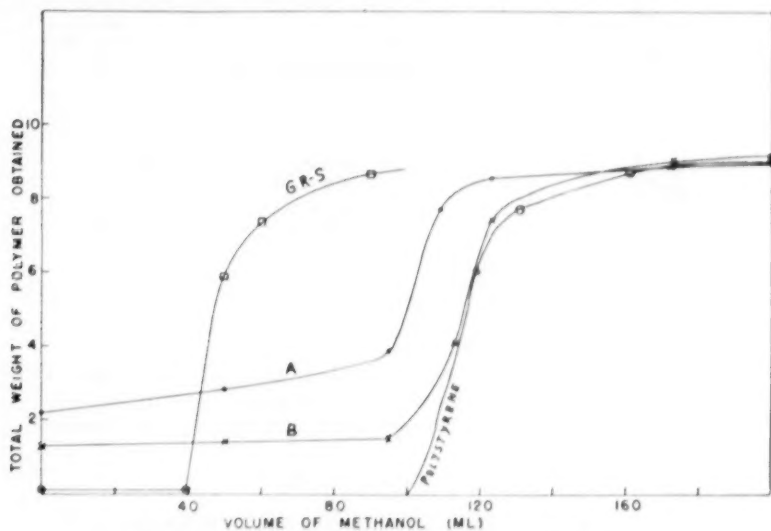


Fig. 1.—Fractionation of graft polymers—styrene on GR-S rubber.

The details of this analytical procedure are given by Kolthoff and Lee⁸ as a method for determining the amount of external (1,2 addition) double bonds in GR-S rubber with an accuracy of ± 3 per cent. This technique is based on the difference in the rates of reaction of 1,2- and 1,4-addition with perbenzoic acid due to the nature of the substituents on the carbon atoms joined by the double bonds. Positive groups such as alkyl expedite the reaction so that internal double bonds (1,4-addition) react faster than the external double bonds. Kolthoff calculated the amount of double bonds oxidized after a specific reaction time, seven hours at 25° C, and used one of three methods⁹ for calculating the amount of external double bonds.

To find the total amount of ethylenic unsaturation directly, we simply allow the reaction to go to completion at room temperature (24 hours is the safe maximum for GR-S) as indicated when no further change in perbenzoic acid concentration, relative to the blank, is shown by titration. A typical experiment is as follows: Place 0.5 g. of the gel fraction, obtained by fractionation of the

whole polymer, in 45 ml. of purified benzene (thiophene-free). An excess of perbenzoic acid solution is added so that this excess of perbenzoic acid over double bonds is not greater than 50 per cent. The amount depends on the molar concentration of the reagent solution and the estimated butadiene composition of the sample. (An estimate of the unsaturation can be made from the infrared method described later and assuming one double bond per mole of butadiene.) A blank with the same concentration of benzene and perbenzoic acid is made at the same time. After twenty-four hours, aliquots of the reaction mixture and blank are analyzed iodometrically⁸. The difference in the number of milliliters of standard sodium thiosulfate solution consumed by the blank and the reaction mixture corresponds to the amount of perbenzoic acid

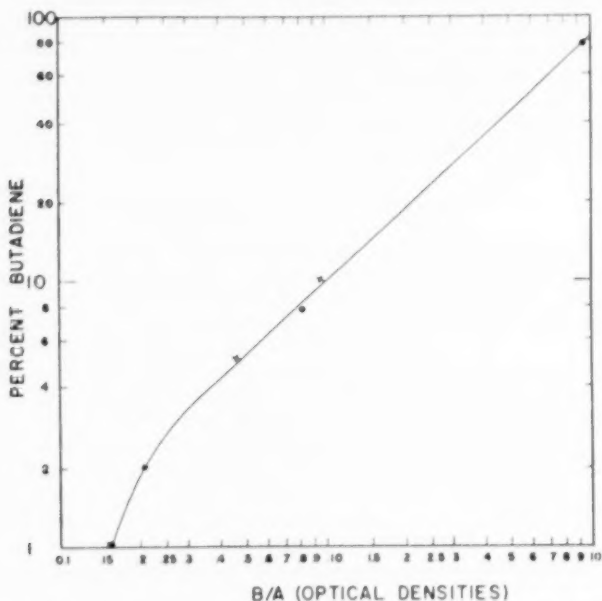


FIG. 2.—Infrared calibration curve for butadiene analysis. $A = 9.73 \mu$. $B = 10.36 \mu$.

consumed in double bond oxidation (1 ml. of 0.1 *N* thiosulfate is equivalent to 0.0069 g. of perbenzoic acid). Titrations can be made at six-hour intervals for different rubber compositions to determine time of complete reaction. Assuming one double bond per mole of butadiene, the percentage unsaturation can then be readily calculated.

Styrene-rubber graft polymers can be handled by the same technique, either as whole polymers or as fractions for determining the percentage unsaturation. Only the gel fractions are here reported.

DETERMINATION OF UNSATURATION (INFRARED)

An infrared technique has been worked out for the approximate analysis of the butadiene-styrene ratio in copolymers, graft polymers, and mixtures. This

method is especially convenient because it can be used on films of unknown thickness. The styrene band at 7.73μ and the butadiene band at 10.36μ were used. A base line was drawn between 8.90 and 10.77μ . The results were calculated from the calibration curve shown in Figure 2. This calibration curve is based on the GR-S rubber used (78.6 per cent butadiene), a mass copolymer containing 7.85 per cent butadiene, mixtures containing 2, 5, and 10 per cent butadiene, and polystyrene.

The results of the infrared analyses for the various fractions are given in Table I. Although the original rubber contained 78.6 per cent butadiene, none of the fractions contained over 18 per cent.

The two gel fractions, A and B, were analyzed independently for unsaturation, using the previously described perbenzoic acid oxidation-thiosulfate titration technique, and the values are shown in Table I. These values are some-

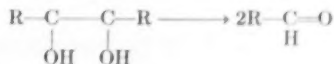
TABLE I
ANALYSIS OF STYRENE-RUBBER GRAFT POLYMERS

Fraction	% Butadiene		Wt. of polystyrene in branches Initial wt. of rubber
	Infrared	Perbenzoic acid (titration)	
A gel	17.7	13.1	3.44
B gel	11.8	7.0	5.66
A-1	16.3	—	3.82
B-1	13.8	—	4.70
A-2	12.5	—	5.28
B-2	16.5	—	3.76
A-3	2.4	—	~33
B-3	4.6	—	~17

what lower than the infrared values, which may be due to differences in the methods or to a change in the double bond content of the gels due to aging since the titration values were obtained some time after the infrared values.

PERIODIC ACID CLEAVAGE

The action of perbenzoic acid on the gel fraction yields a product containing adjacent hydroxyl groups. Materials with this structure can be cleaved by periodic acid, a specific 1,2-glycol splitting agent, to yield degradation products with aldehyde or carboxy end groups:



The present experiment would give polystyrene chains with aldehyde or carboxy end groups. The hydroxylated fractions were cleaved with periodic acid at the double bonds in the original material to give low molecular weight methanol-soluble end-products from the GR-S rubber according to the following experimental procedure. A sample of the hydroxylated polymer, styrene-rubber gel fraction, was weighed into a clean flask (approximately 0.5 g.) and dissolved in dioxane. The calculated amount of $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in water and added to the original solution so that the final solution was about 90 per cent dioxane. The flask was allowed to stand for twenty-four hours and warmed to about $60-70^\circ \text{C}$ for thirty minutes at the end of this time. The

TABLE II
CLEAVAGE DATA OF A AND B GEL

Sample	Gel A	Gel B
Weight (g.)	0.5152	0.5030
Weight hydroxylated (g.)	0.4549	0.4401
Weight after cleavage (total) (g.)	0.3363	0.3400
Weight polystyrene chains (g.)	0.2553	0.2668
Intrinsic viscosity, $[\eta]$, (dl./g.)	0.490	0.330
M_w	160,000	96,000

solvents were removed at reduced pressure and the dry residue washed with dilute base. The solid was then dried in a vacuum desiccator, weighed, and dissolved in 30–40 ml. of methylethyl ketone. Any insoluble material was removed by filtration and the ketone soluble portion precipitated with methyl alcohol. These products showed carbonyl bands and no unsaturation by infrared analysis and the intrinsic viscosities were determined on these polystyrene fractions after reprecipitation. The molecular weight of these side chains was determined by intrinsic viscosity measurements in methylethyl ketone from the equation²:

$$[\eta] = 3.05 \times 10^{-5} \bar{M}_w^{0.802}$$

The calculated results are given in Table II. The molecular weight of the polystyrene side chain was 160,000 for the A gel and 96,000 for the B gel.

DISCUSSION OF RESULTS

On the basis of the fractionation data alone, a difference between materials A and B is clearly shown and a considerable amount of grafting of styrene onto

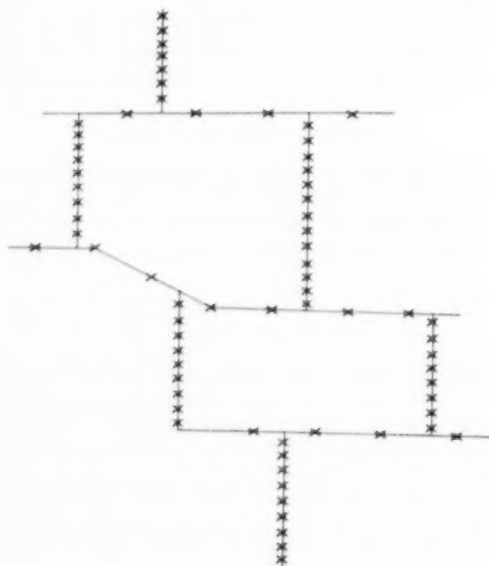


FIG. 3.—Structure of styrene grafted onto GR-S rubber—A and B gels: (x) styrene monomer units; (—) butadiene monomer units.

rubber is also indicated. Most of the grafted material appeared in the gel portion and the first two fractions. The other fractions were mostly polystyrene. The grafted material was milky in appearance. Both A and B contained about 2.5 times as much gel as there was rubber originally added (the original rubber contained only about 1 per cent gel). The B gel settled out more rapidly than the A gel, indicating a more tightly crosslinked material.

It is assumed the structure of these gels is similar to that shown in Figure 3. For such a model, the A gel has polystyrene chains that serve as crosslinks that are 1530 monomer units long. The number of rubber monomer units (average molecular weight = 60) in the rubber chains between crosslinking chains is about 267. For the B gel, the polystyrene chains acting as crosslinks contain

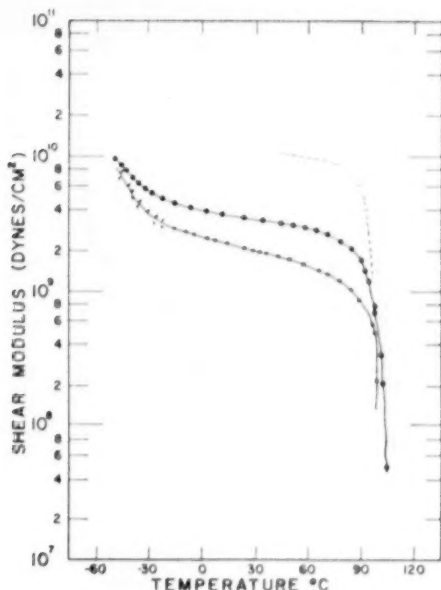


Fig. 4.—Dynamic shear modulus of: (X) A gel; (●) A1f1; (---), polystyrene.

918 monomer units while the number of rubber monomer units between crosslinked points is 73. These values are based upon the titration values of the butadiene content. If the infrared values are used instead, the number of rubber monomer units between crosslinks is 385 and 141 for the A and B gels, respectively. The B gel is the more tightly crosslinked structure, in agreement with observed swelling characteristics.

Dynamic mechanical tests were made on the A gel and a soluble milky fraction A1f1 similar to A-1 in composition. Figures 4 and 5 compare the dynamic properties of the graft polymers with polystyrene.

The mechanical damping of the graft polymers shows two peaks. The peak at about 100°C is characteristic of polystyrene while the low temperature peak is characteristic of a rubber¹⁰. The grafting has shifted the damping peak

of the rubber from -65 or -70°C for the GR-S rubber to -40°C in the graft. The graft polymer acts like a mixture of two polymers but they cannot be separated into distinct phases because of the chemical bonds connecting the polystyrene chains to the rubber molecules. Both the milky appearance and the two damping peaks indicate that the polystyrene and the rubber segments try to separate from one another and to aggregate with themselves. The A_{1f1} fraction has a higher modulus and lower damping peak for the rubber phase than the A gel. This is to be expected, since the analyses indicate the A gel has the higher butadiene content.

Mechanical measurements were not made on the graft polymer fractions obtained from the B material because of insufficient quantities. Dynamic

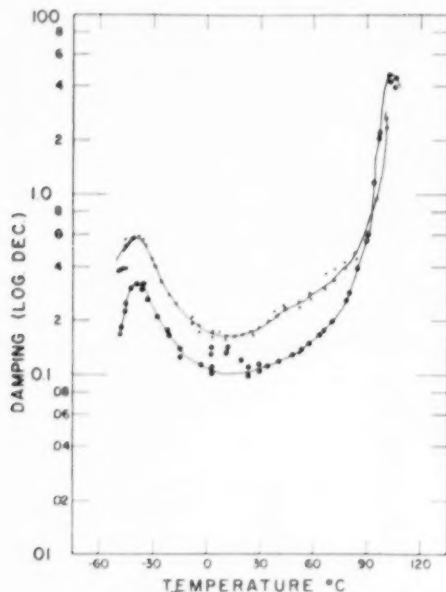


Fig. 5.—Mechanical damping of: (X) A gel; (●) A_{1f1} .

tests had been made on the starting material and it can be concluded that the B gel should have a higher modulus than the A gel. The B gel had a transition (damping peak) at -1°C , compared with the -65 to -70°C for the GR-S rubber. This is to be expected from the higher grafting and degree of cross-linking found in the B gel.

SYNOPSIS

Two styrene-rubber polymers were prepared by mass polymerization and fractionated to isolate the insoluble graft portions of each. These graft fractions were analyzed by two methods (titration and infrared) for unsaturation. Cleavage at the hydroxylated double bonds was carried out and the polystyrene chains were isolated. A diagrammatic structure for the insoluble graft material

has been calculated from the length and number of the polystyrene chains isolated by the cleavage technique. The physical and mechanical properties of the gel fractions are reported.

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CHAIN SCISSIONS IN A POLYMER NETWORK *

M. M. HORIKX

RUBBER-STICHTING, DELFT, THE NETHERLANDS

INTRODUCTION

Relations between degree of crosslinking and gel fraction in a polymer have been derived by several authors¹. An important parameter in these relations is the crosslinking index γ , the average number of crosslinks to which one original polymer molecule is linked. The relations have been applied to the determination of the degree of crosslinking in linear polymers, but they can be used as well to calculate the soluble fraction of the network in a crosslinked polymer that has been subjected to a degradation process.

It will be shown in this paper that a simple relation exists between the soluble fraction of a network that has undergone scission and the effective number of chains in the gel fraction (as determined by swelling measurements). The fraction of soluble material in the degraded network is a measure of the number of scissions.

This problem bears upon natural-rubber vulcanizates, which give increasing amounts of extractable material and increasing degrees of swelling on the absorption of oxygen.

THEORETICAL CONSIDERATIONS

A three-dimensional network, formed from a linear polymer by a random crosslinking process, is subjected to a scission reaction. Three limiting cases will be distinguished as (a) chain scission at random; (b) severance of the crosslinks; and (c) directed scission.

CHAIN SCISSION AT RANDOM

Both scissions and crosslinks are distributed at random; the final state of the polymer will be independent of the order in which the two treatments have been applied. The number of crosslinks remains constant; each monomer unit in the chain between crosslinks (and in the loose ends) is equally likely to undergo scission.

This case can be treated if the crosslinking and scission reactions are formally interchanged. The required number of chain scissions is randomly applied to the unvulcanized polymer, after which the crosslinks are brought into the same positions they would have occupied if no scission had taken place (i.e., they are distributed at random among all monomer units of all polymer molecules).

If the chain scission has been a random process, the chain length distribution² is represented by:

$$N_x = N\beta (1 - \beta)^{x-1} \quad (1)$$

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which can be approximated by:

$$N_x = N\beta e^{-\beta x} \quad (1a)$$

in which $1/\beta$ = number-average length of the fragments, N_x = number of fragments with length x , N = total number of fragments, and x = number of monomer units in a fragment.

It has been shown by Charlesby¹ that in a polymer with this chain length distribution after a crosslinking process in which each crosslink connects two monomer units of different molecules, the soluble fraction is given by:

$$s = \frac{(2 + \gamma) - (\gamma^2 + 4\gamma)^{1/2}}{2\gamma} \quad (\gamma \geq 0.5) \quad (2)$$

(which is the explicit form of his Equation 7), in which γ = crosslinking index of the whole polymer = average number of crosslinked units per original chain (or average length $1/\beta$).

It is evident that the relation:

$$\gamma = \nu_0/N \quad (3)$$

holds. Here $1/2 \nu_0$ = number of crosslinks per gram of polymer, and N = number of primary molecules per gram of polymer (after the scission reaction).

It can also be shown¹ that the number-average molecular weight of the primary molecules, incorporated in the gel, is given by:

$$M_{gel} = M_0[(1 + \gamma - \gamma s)/\gamma] \quad (4)$$

if M_0 = number-average molecular weight of *all* primary molecules, and that the cross linking index of the gel fraction is equal to:

$$\gamma_{gel} = (1 + s)(1 + \gamma - \gamma s) \quad (5)$$

It follows from (4) that the number of primary molecules in 1 gram of network polymer is given by:

$$N_{gel} = \frac{\gamma N}{1 + \gamma - \gamma s} = \frac{\nu_0}{1 + \gamma - \gamma s} \quad (6)$$

and it is easily shown from (3), (5), and (6) that the number of "ideal chains" in the network polymer ν_{0gel} (twice the number of crosslinks in the gel) is given by:

$$\nu_{0gel} = \gamma_{gel} N_{gel} = \nu_0 (1 + s) \quad (7)$$

i.e., the number of crosslinks in 1 gram of gel is larger than the corresponding number in the whole polymer by a factor of $(1 + s)$. The number of "ideal chains" is the number of unbroken chains between crosslinks if M_0 of the initial polymer is infinite. From the relation between s and γ , in the form given by Charlesby¹;

$$s = 1/(1 + \gamma - \gamma s)^2 \quad (8)$$

it follows that (6) can be written as:

$$N_{gel} = \nu_0 s^{1/2} \quad (9)$$

The effective number of chains per gram of polymer in a crosslinked polymer is given by^{1,2}:

$$\nu_e = \nu_0 - 2N \quad (10)$$

(valid for a tetrafunctional network) where ν_e is the number of chains appearing in the swelling relation:

$$\ln(1 - v_2) + v_2 + \mu v_2^2 + \nu_e(\rho V_1)v_2^{\frac{1}{2}} = 0 \quad (11)$$

where v_2 = volume fraction of polymer in the swollen state, ρ = density of the polymer, V_1 = molar volume of the solvent, and μ = interaction parameter for the polymer-solvent system.

The effective number of chains in 1 gram of gel is given by:

$$\nu_e = \nu_{\text{gel}} - 2N_{\text{gel}} = \nu_0(1 + s) - 2\nu_0 s^{\frac{1}{2}}$$

or:

$$\nu_e = \nu_0(1 - s^{\frac{1}{2}})^2 \quad (12)$$

If, during the degradation reaction, ν_0 (i.e., the total number of crosslinks) is constant, the relation sought between soluble fraction and relative decrease in the effective number of chains (in the gel fraction) in a three-dimensional polymer is:

$$1 - \frac{\nu_{e2}}{\nu_{e1}} = 1 - \frac{(1 - s_2^{\frac{1}{2}})^2}{(1 - s_1^{\frac{1}{2}})^2} \quad (13)$$

in which s_1 = soluble fraction in the undegraded crosslinked polymer, and ν_{e1} = effective number of chains before degradation; s_2 and ν_{e2} are the corresponding quantities in the degraded polymer. (It has been assumed that the portion of the polymer not connected with the infinite network can be wholly extracted from the gel fraction, and thus can truly be labeled as the soluble fraction.)

Obviously the number of chain scissions in 1 gram of polymer is given by:

$$n = N_2 - N_1 = \nu_0(1/\gamma_2 - 1/\gamma_1) \quad (14)$$

In Equation (14), subscript 1 indicates the whole polymer before the chain scission reaction and subscript 2 the whole polymer after the scission.

SEVERANCE OF THE CROSSLINKS

If there is no chain scission, but only opening of the crosslinks, the number of primary molecules remains constant and:

$$\nu_e = \nu_{\text{gel}} - 2N_{\text{gel}} = \nu_0(1 - s^{\frac{1}{2}})^2 = N\gamma(1 - s^{\frac{1}{2}})^2 \quad (15)$$

if it can be assumed that in the initial polymer the chain length distribution is given by (1). (In a natural rubber vulcanizate this probably holds as a consequence of the degradation on the mill.)

N is constant in this case, but the number of crosslinks ($= 1/2 \nu_0$) decreases. Then the relation between effective number of chains in the gel fraction and soluble fraction is:

$$1 - \frac{\nu_{e2}}{\nu_{e1}} = 1 - \frac{\gamma_2(1 - s_2^{\frac{1}{2}})^2}{\gamma_1(1 - s_1^{\frac{1}{2}})^2} \quad (16)$$

This relation is very sensitive to the value of γ_1 = crosslinking index of the vulcanizate before the scission reaction, in contrast to (13), which is insensitive to γ_1 .

The number of scissions is equal to the number of disengaged crosslinks. It is:

$$N = \frac{1}{2} (\nu_{01} - \nu_{02}) = \frac{1}{2} N (\gamma_1 - \gamma_2) \quad (17)$$

(again γ_1 and γ_2 of the whole polymer).

DIRECTED SCISSION

In directed scission, only those monomer units that are the nearest neighbors to a crosslink can undergo scission. As a result of this directing influence, the formal interchange of the crosslinking and scission reactions cannot be applied in the same manner as in random scission. Only qualitative conclusions can therefore be drawn in this case.

An arbitrary portion of the three-dimensional network will be considered, consisting of a small number of chains between crosslinks (say n), part of this network portion having been cut off from the infinite network as a result of the scission reaction. The weight of the soluble fragment thus formed is clearly proportional to the length of the chains in the network portion. The probability that a sufficient number of scissions will have occurred to disconnect this soluble fragment from the entire network will be proportional to the number of crosslinks in the arbitrary portion (i.e., proportional to m), if the scissions were directed by the crosslinks.

In the case of random scission, however, the probability of a sufficient number of scissions will be proportional to the total number of monomer units in the portion, consisting of m chains, i.e., the probability in the latter case will be proportional to m times the length of the chains.

In the former case (directed scission), the weight loss of the arbitrary network portion, caused by a given number of chain scissions in the entire network, will be proportional to the number-average chain length in the arbitrary network portion; in the latter case (random scission), the same number of chain scissions in the entire network will cause a weight loss in the arbitrary portion that is proportional to the weight-average chain length of the arbitrary portion of the network.

The loss in elastically active chains $1 - (\nu_{e2}/\nu_{e1})$ depends only on the total number of chain scissions.

It can be stated, therefore, as a rough approximation, that the weight of the soluble fraction at a given value of $1 - (\nu_{e2}/\nu_{e1})$ in the case of directed scission is about half this amount for random scission, as the distribution of chain lengths probably obeys (1), for which $\bar{M}_w = 2\bar{M}_n$. The complete quantitative treatment of the problem of directed scission cannot yet be given, as the formal reversal of scission and crosslinking, which greatly simplified the problem, cannot be applied.

The approximate relation between number of effective chains and soluble fraction will therefore be:

$$s_2 \cong \frac{1}{2} \left[1 - (1 - s_1^{\frac{1}{2}}) \left(\frac{\nu_{e2}}{\nu_{e1}} \right)^{\frac{1}{2}} \right]^2 \quad (18)$$

or:

$$1 - \frac{\nu_{e1}}{\nu_{e2}} \cong 1 - \frac{[1 - (2s_2)^{\frac{1}{2}}]^2}{[1 - s_1^{\frac{1}{2}}]^2} \quad (18a)$$

It must be stressed, however, that (18) or (18a) are only very approximate, as the intricate interplay between crosslink and chain length distributions, and the distribution of crosslinks between sol and gel have been neglected. Therefore conclusive evidence cannot be based on Equations (18) and (18a). It can be expected that at higher values of $1 - (\nu_{e2}/\nu_{e1})$ the value of s_2 will be higher than represented by (18), as the weakly crosslinked portion of the network will have gone into solution and the preference for the long chains, present in random scission but absent in directed scission, has lost some of its importance.

EXPERIMENTS

Numerical data that are available originate from oxygen-absorption experiments with natural rubber sulfur-Santocure vulcanizates.

Composition	Parts by weight
Smoked sheet	100
Zinc oxide	5
Stearic acid	1
Sulfur	2
Santocure	1
Antioxidant	Variable
Cure 20 min. at 142° C	

The effective number of chains has been computed from swelling measurements in chloroform with the help of Equation (11), taking $\mu = 0.30$ (determined by comparison of the swelling in benzene and in chloroform of several samples of natural-rubber vulcanizates, and using a value of $\mu = 0.395$ for the rubber-benzene system).

After swelling at room temperature for 24 hours, the samples (thickness 1 mm.) were heated in vacuo at 100° C to constant weight, from which the loss in weight follows after correction for the content of extractable nonrubber components of the vulcanizate. As, after swelling for 24 hours, both degree of

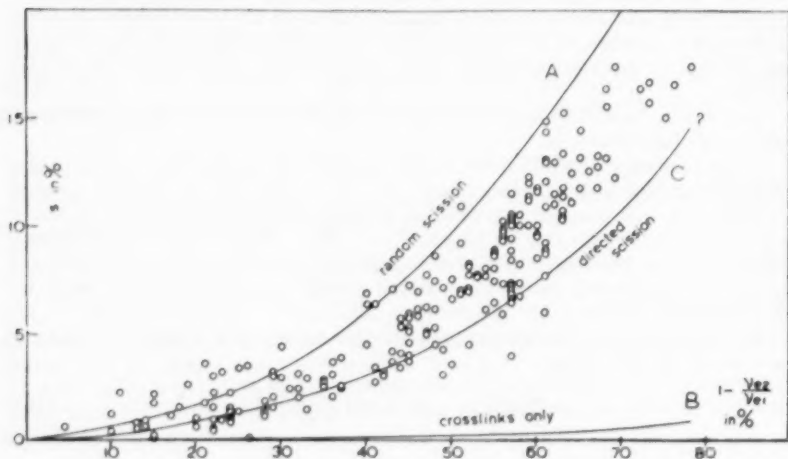


FIG. 1.—Weight loss in a degraded natural rubber network as a function of the percentage of the inactive chains.

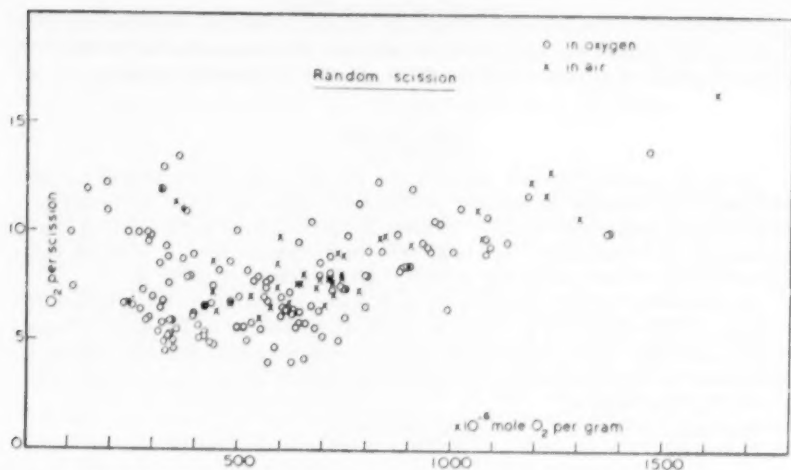


Fig. 2.—Number of oxygen molecules per scission in a natural rubber vulcanizate as a function of the total amount of oxygen absorbed.

swelling and weight loss had become constant, it was assumed that the whole sol fraction was extracted during the swelling procedure.

The experimental results are given in Figure 1, in which the soluble fraction s is given as a function of the relative decrease in number of effective chains. These results originate from oxygen absorption experiments in pure oxygen and in air, mostly at 100°C , in the absence or presence of varying amounts of antioxidant and in the absence or presence of various metal stearates (Cu, Co, Fe, Mn, Ni, Zn, Pb, Al, Cr, Cd, Ti) that had been applied by a swelling method similar to that of Chovin⁴.

The calculated curves A , B , and C are constructed with the help of Equations (13), (16) and (18a), respectively, using the following values of the parameters: $N = 5 \times 10^{-6}$ mole/g., $\nu_0 = 200 \times 10^{-6}$ mole/g. Therefore: $\gamma_1 = 40$ and $s_1 = 0.0006$ (0.06%), corresponding to a natural rubber vulcanizate of initial molecular weight $M_0 = 200,000$ and average molecular weight between crosslinks $M_c = 5000$ (the data for the undegraded vulcanizate are: swelling in benzene ~ 320 weight per cent, in chloroform ~ 710 weight per cent; retractive force at 100 per cent elongation ~ 10 kg./cm.² original cross-section at room temperature).

The only parameter in Equation (13) is s_1 ; s_2 , ν_{e1} and ν_{e2} are experimental quantities. s_1 cannot be determined directly because of the soluble nonrubber components in a vulcanizate. $s_1 = 0.0006$ corresponds with the given values of N and ν_0 , and depends only on the ratio ν_0/N . Equation (13), however, is very insensitive to the assumed value of ν_0/N as long as $\nu_0/N > 10$.

The exact value of M_0 is therefore unimportant. The value $M_0 = 200,000$ is based on the intrinsic viscosity of a normally plasticized natural rubber in toluene, for which has been found $[\eta] \sim 1.8$ dl./g. (Equation 16, on the other hand, would be very sensitive to the assumed value of ν_0/N .)

For the samples indicated in Figure 1, the total amount of oxygen absorbed was determined by the van Amerongen method⁵.

Figure 2 gives the average-number of oxygen molecules absorbed on each chain scission (which is simply the ratio of moles of oxygen absorbed to moles of chain scissions) as a function of the total amount of absorbed oxygen.

DISCUSSION

As can be seen in Figure 1, the relation between soluble fraction of the network and the decrease in number of effective chains is of the character predicted for scissions in the chains; the inference is that there is no question of any breaking of the crosslinks. It has already been stressed that a different value of the ratio ν_0/N has hardly any influence on the course of curve A.

As curve C is highly speculative, it is not possible to decide whether the scissions in the chain are at random or whether there is a directing influence of the crosslinks. In a sulfur-cured natural rubber, such an influence would be reasonable, as the oxidizability of the vulcanizate is known to be greater than that of the raw rubber.

The number of chain scissions is given by:

$$n = N_2 - N_1 \quad (14a)$$

and this number can be compared with the amount of oxygen absorbed by the sample. n is calculated with the assumption of random chain scission; then the soluble fraction s_2 is related to γ_2 of the whole polymer by means of Equation (2). Equation (3) gives the relation between γ_2 and N_2 ; then (14) gives the number of chain scissions n .

In Figure 2, the average number of oxygen molecules absorbed for each chain scission is given as a function of the total amount of oxygen taken up by the sample. Circles represent oxidation in pure oxygen and crosses, oxidation in air, both at atmospheric pressure. The oxygen absorption was measured at 100° C; the antioxidant was Age-Rite Alba (monobenzyl ether of hydroquinone) in varying amounts; and various catalyzing or noncatalyzing metal stearates in amounts of 0-1 per cent were present. The results show that on the average 5-10 molecules of oxygen are needed for each chain scission; a correlation with rate of oxidation or oxygen pressure could not be found. It has been stated that, during stress relaxation of a natural rubber pure gum vulcanizate at 100° C, one scission occurs to every 5 absorbed oxygen molecules⁶ and that, during oxidation of the closely related hydrocarbon gutta-percha in solution at 100° C, 15-20 molecules of oxygen are needed for each chain scission⁷.

It is not certain whether the rise in number of oxygen molecules per scission with increasing oxygen absorption is significant, as the relations for random scission are used in the computation, although the experiments do not show full agreement with this assumption; this is evident from Figure 1. But it can safely be concluded that, in the oxidation of a Santocure-sulfur natural rubber vulcanizate at 100° C under various conditions, there exists substantial discrepancy between the number of oxygen molecules absorbed and the number of chain scissions caused by the oxygen. Chain scission during the oxidation must be a side reaction, but occurring in an almost constant ratio to the main reaction (the oxygen absorption).

The nature of this scission reaction is as yet obscure. The main reaction probably follows the oxidation scheme proposed by Bolland⁸, but in this and similar oxidation schemes scission reactions are not accounted for.

ACKNOWLEDGMENT

This work forms parts of a program of fundamental research on rubber oxidation, undertaken by the Research Department of the Rubber-Stichting, Delft, Netherlands, under the management of H. C. J. de Decker.

SYNOPSIS

Relations between the soluble fraction and the number of effective chains between crosslinks in a three-dimensional network undergoing a scission reaction have been derived. Three limiting cases have been considered: (a) random scission in the chains, (b) scission in the chains directed by the crosslinks, and (c) scission of the crosslinks. The number of scissions can be computed from the fraction of soluble material in a degraded network, determined experimentally. This procedure has been applied to the oxidation of a natural-rubber vulcanizate. In a natural rubber-sulfur-Santocure vulcanizate, the scission reaction accompanying the oxygen absorption at 100° C does not involve opening of the crosslinks, but it remains undecided whether the scission in the chains is directed or at random. At each chain scission about 5–10 molecules of oxygen are taken up by the rubber at 100° C under various conditions, this number being apparently independent of the rate of oxidation, the absence or presence of anti-oxidants and metal stearates as catalysts, and the oxygen pressure.

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MECHANICAL METHOD OF DETERMINATION OF THE VITRIFICATION TEMPERATURE OF RUBBERLIKE POLYMERS *

A. I. MAREI

It is known that, on lowering the temperature, rubberlike polymers lose their elastic properties and are converted to the solid state. Like the transition of a supercooled liquid to the vitreous state, such a type of solidification of the polymers is accompanied by no phase transitions.

For some rubberlike polymers (natural rubber, polychloroprene, etc.) it is also possible to observe solidification in a definite temperature range as a result of incomplete crystallization. However, for these polymers also, even in such a partially crystalline state, there is a temperature region of transition to the solid amorphous state of the noncrystallized phase.

According to modern concepts, the high elasticity and the low modulus of rubberlike polymers are brought about by a relaxation mechanism of rearrangement of the elements of the polymer structure during the deformation process, with retention of the average distances between them.

As a result of the weak interaction of the chain macromolecules of rubberlike substances at normal temperatures (quasi-liquid state), the individual portions of the molecules are able to rearrange during the imposition of an external field. However, on lowering the temperature, the decrease of the thermal energy of the molecules leads to an increase of interaction among the elements of the polymer structure. This is indicated by the fact that deformation of the polymer does not increase with stress, and equilibrium deformation is not attained at once, but only after a certain time interval, which increases exponentially with reduction of the temperature. Establishment of this law of change of the elastic deformation in relation to temperature and time should be credited to Kobenko¹, Aleksandrov², and other investigators, and is an important contribution to the science of the mechanical properties of polymeric substances.

At sufficiently low temperatures, the time of establishment of equilibrium deformation becomes incommensurably large compared with the time of the mechanical action, and the polymer acquires the properties of a solid.

A reduction of the temperature leads to a decrease of the specific volume of the polymer, because of the drawing together of the molecules (as in ordinary solids), and leads to changes of the mutual orientation of the individual parts of the molecules (maximum packing). The capacity of the elements of the macromolecules for orientation rearrangements determines the high value of the temperature coefficient of expansion of the polymeric substances in the rubberlike state.

In proportion to the decrease of temperature, rearrangements of the parts of the macromolecules are retarded as a result of the rapidly increasing viscosity of the system. In the long run, the polymer structure "freezes", and, with

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more thorough cooling, an increase of the density of the polymer proceeds only because of a decrease of the average distances between the molecules. Therefore, a sharp change of the temperature effect of the specific volume of the polymer sets in during the process of freezing of the structure. The value of the coefficient of volumetric expansion changes sharply in the vitrification temperature range. Moreover, the heat capacity and other physical characteristics of the polymer, for example, the mechanical, electrical, and optical properties,



Fig. 1.—General view of the apparatus for the determination of vitrification temperature of rubberlike polymers.

connected with the change of mobility of the elements of the polymer structure, also change sharply. It is clear that the temperature dependence of any of these characteristics may serve as a criterion for the determination of the vitrification temperature of the polymer.

The fixation of the polymer structure does not come at a strictly definite temperature, as, for example, in the crystallization of low-molecular substances, but occurs in a certain temperature interval; therefore, the vitrification point of the polymer depends on the method of determination. The vitrification temperature T_v of the polymer, determined from the change of the temperature

effect of the specific volume, depends on the rate of cooling; and the more rapid the cooling, the higher it is. Again, a greater discrepancy in the vitrification temperature values may be obtained from the mechanical characteristics of the polymer in the vitrification region. An increase of the frequency of imposition of the force increases the vitrification temperature of the polymer, whereas a static stress leads to lower T_g values. Hence, it follows that the temperature-time dependence of the change of the polymer to the solid vitreous state should strictly be considered in the methods of measurement of T_g .

Nevertheless, in the determination of the vitrification temperature there is some uncertainty about the nature of the process itself; this temperature is an important characteristic both in the evaluation of the technical properties of the polymers (freeze resistance of rubbers) and in the study of their structure.

It was stated above that the determination of the vitrification temperature of the polymers may be made by any method which establishes the temperature dependence of the relaxation time of the polymer. These methods are: (1) the dilatometric method, i.e., measurement of the specific volume during slow cooling of the polymer; (2) the calorimetric method, i.e., determination of the temperature dependence of the heat capacity in the vitrification region of the polymer; (3) the refractometric method, i.e., measurement of the index of refraction of the polymer at different temperatures; and (4) the mechanical method, i.e., determination of the temperature dependence of the elastic deformation of the polymer.

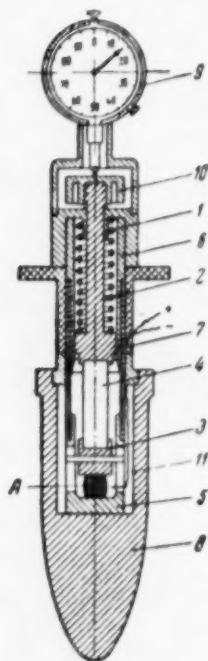


FIG. 2.—View (in cross-section) of the apparatus for determination of vitrification temperature.

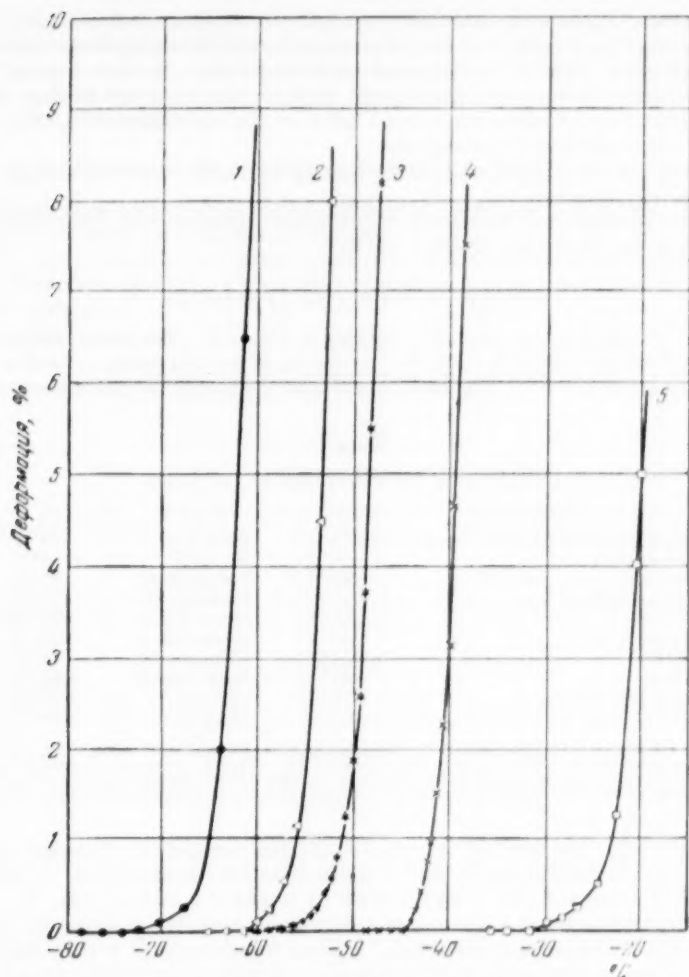


Fig. 3.—Deformation of rubberlike polymers in the vitrification region: 1—Natural rubber; 2—Buna S-3; 3—SK-B; 4—Neoprene; 5—Buna SS. The ordinate indicates the deformation, in percentage; the abscissa the temperature in °C.

The first two methods are characterized by their complexity and low efficiency. The refractometric method is used only for clear and carefully purified polymers, which limits its application.

The determination of the vitrification temperature of polymers by the mechanical method is based on the measurement of the deformation of a slowly heated supercooled polymer sample, under the action of a constant compressive stress.

The temperature of the transition of the polymer to the vitreous state does not depend on its molecular weight³.

On lowering the temperature, first of all, the plastic deformation is hampered as a result of the formation of a small number of stable secondary bonds between the individual parts of the adjacent macromolecules. In such a state, the polymer is similar to vulcanized rubber. Only on more thorough cooling, when a large number of bonds are formed between the macromolecules, does the highly elastic deformation disappear.

Thus, the deformation of a polymer, measured in the vitrification region, is of an elastic nature.

The vitrification temperatures of rubberlike polymers were determined by the apparatus shown in Figures 1 and 2.

DESCRIPTION OF THE APPARATUS

The principle of the apparatus is shown in Figure 2. The stress, which acts on the polymer sample A, is applied by means of a spiral spring 1, fixed in the base of a guide screw 2. The spring presses on the base of the guide screw with

TABLE I
VITRIFICATION TEMPERATURES OF POLYMERS

Polymer	T_v	Polymer	T_v
Natural rubber (smoked sheet)	-71° C	Buna S-3	-60° C
Kok-saghyz	-66° C	Buna-SS	-30° C
Guayule	-66° C	Perbunan-26	-43° C
Gutta-percha*	-71° C	Perbunan-35	-32° C
Buna-65	-65° C	Hycar OR-25	-36° C
Buna-32	-52° C	Hycar OR-15	-23° C
SK-B	-54° C	Neoprene-M	-44° C
GR-S	-64° C	Butyl rubber	-69° C
Buna SW-10	-75° C	Oppanol	-70° C
		Vistanex	-70° C

* The vitrification temperature of gutta-percha was determined by rapid supercooling in liquid air of a polymer sample heated to 80° C in order to avoid crystallization. The polymer samples supercooled in this way vitrified at lower temperatures than those shown in the table. The vitrification temperature of gutta-percha, given in the table, was the relative value corresponding to the test conditions adopted.

a force of 5 kg. In order to decrease the thermal conductivity from the upper part of the apparatus to the lower, which is at low temperatures, the guide screw 2 is connected with a copper cap 3 by means of a glass cylinder 4. For this purpose the lower 5 and upper 6 detachable sockets are connected by a thermally insulating porcelain tube 7. The lower detachable socket, made of cuprite, has an open port for centering the polymer on the copper cap of the guide screw.

The outer copper socket 8 serves for uniform cooling of the sample and for its insulation from contact with the cooling mixture.

The deformation of a polymer sample is observed by reading the indicator of the micrometer gauge 9, fixed in the upper part of the apparatus. The value of a micrometer gauge division is equal to 0.01 mm. The jaw of the micrometer is fixed in the covering nut 10 of the guide screw. The accuracy of the deformation reading of the sample exceeds ± 0.05 per cent, which is entirely adequate for determination of the vitrification temperature of the polymer with an accuracy of about $\pm 1^\circ$, under conditions of the observance of the established rate of heating of the sample.

The temperature of the sample is registered by a sensitive thermocouple 11.

The end of the thermocouple is fastened at an angle to the surfaces of the lower detachable socket near the sample.

Figure 3 shows typical curves of the temperature dependence of the compression deformation of rubberlike polymers in the vitrification region under the action of a constant stress.

VITRIFICATION TEMPERATURE OF RUBBERLIKE POLYMERS

Vitrification temperature values of rubberlike polymers, obtained by means of the mechanical method, are presented in Table I.

The vitrification temperature values of the polymers, obtained by means of the mechanical method, did not differ practically from the values found by other methods.

TABLE II
VITRIFICATION TEMPERATURES OF POLYMERS,
ESTABLISHED BY DIFFERENT AUTHORS

Polymer	T_g (°C)	Method of measurement	Authors
Natural rubber	-73°	Dilatometric	Bekkedahl and Matheson ⁴
	-73°		
	-70°	Calorimetric	Ruhemann and Simon ⁵
	-67°		
	-71°	Interferometric	Wood, Bekkedahl, and Peters ⁴
Polyisobutylene	-71°	Mechanical	Our data
	-74°	Dilatometric	Ferry and Parks ⁷
	-74°		
	-70°	Calorimetric	Our data
	-70°		
Oppanol	-70°	Mechanical	Our data
Vistanex	-70°		
Butyl rubber	-69°		
GR-S	-59°	Calorimetric	Rands, Ferguson, and Prather ⁸
	-64°	Mechanical	Our data
	-64°		
Hycar OR-25	-37°	Refractometric	Wiley and Brauer ⁹
	-36°	Mechanical	Our data
Hycar OR-15	-23°	Calorimetric	Bekkedahl and Scott ¹⁰
	-26°	Refractometric	Wiley and Brauer ⁹
	-23°	Mechanical	Our data

Comparative data on the vitrification temperatures of several polymers, established by different authors, are presented in Table II.

It was stated above that the T_g determinations of the polymers, based on the measurement of the heat capacity, coefficient of expansion, or index of refraction of the polymers in the vitrification temperature region, are characterized by lengthiness and by relative complexity. The mechanical method eliminates these disadvantages, and therefore is of much interest in the study of the temperature interval of elasticity of the polymers.

CONCLUSIONS

1. A mechanical method has been developed for the determination of the vitrification temperature of rubberlike polymers, based on measurement of the compression deformation of polymer samples in the vitrification temperature region under a constant stress.

2. An apparatus for the determination of the vitrification temperature of polymers by the mechanical method is described.

3. The vitrification temperatures of a series of polymers have been determined. The agreement of results of the determination of the vitrification temperature of the polymers by mechanical and by other methods is shown.

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THERMODYNAMICS OF CRYSTALLIZATION IN HIGH POLYMERS. GUTTA-PERCHA *

L. MANDELKERN, F. A. QUINN, JR., AND D. E. ROBERTS

RUBBER SECTION, NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.

INTRODUCTION

Statistical and thermodynamic methods describing the fusion process of semicrystalline polymers have been developed in recent years¹ and the major deductions of the theory have been substantiated by experiment². The theoretical analysis has indicated that, due to the nature of a semicrystalline polymer, the significant thermodynamic parameters are those which are characteristic of the structural repeating unit. Thus an equilibrium melting temperature T_m^0 is defined as that at which the most perfect crystallites are unstable relative to the pure polymeric liquid and is representative of the melting temperature of a macroscopic perfect crystal. Similarly, it is of great utility to consider the heat and entropy of fusion characteristic of the transformation of polymer repeating units from the crystalline to liquid state rather than the quantities applicable to the transformation of the entire semicrystalline polymers. These latter quantities will obviously depend on the relative amounts of crystalline and noncrystalline material in the system. To determine melting temperatures which are of thermodynamic significance, it is necessary to employ slow heating rates³ so that sufficient time is allowed for the formation of the more perfect crystallites.

The thermodynamic parameters governing the crystallization behavior of natural rubber, *cis*-polyisoprene, have recently been deduced⁴, and it is of interest to compare these results with those for gutta-percha, a *trans*-polyisoprene. A study of the crystallization behavior of gutta-percha is complicated by the existence of several crystalline modifications. Two of them occur without the application of any external stress⁵, while a third recently discovered polymorph occurs only when the polymer is deformed⁶. The polymorphism of gutta-percha together with the usual difficulties of establishing equilibrium conditions in a semicrystalline polymer have made past interpretation of the volume-temperature relations difficult⁷. However, since it has been deduced from studies on other polymers that equilibrium conditions can be approached by using slow heating rates, the adoption of this procedure has aided in clarifying the analyses of the data for gutta-percha. Furthermore, an analysis of the melting of each of the forms can help establish thermodynamic criteria for their relative stability without recourse to kinetic observations, as has been necessary in the past⁸. We shall be concerned solely with the two crystalline modifications which can occur without the application of external stress. To avoid confusion in their identification we shall term them the low-melting form (LMF) and the high-melting form (HMF) which correspond to the β - and γ -forms, respectively, in Fisher's terminology⁶.

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EXPERIMENTAL

A cake of gutta-percha was received in a vacuum tin from the Tjipeti Rubber Plantation in the Netherlands Indies and was stored in a dry-ice chest prior to use. Since a preliminary analysis indicated the sample to contain only about 94 per cent hydrocarbon, further purification was deemed advisable. A portion of the sample was passed through a dry wash-mill several times in order to form a sheet, and then about 80 g. of the gutta-percha was extracted with freshly distilled acetone for about 135 hours. The extraction process was conducted in the absence of light, as much as feasible, and periodically interrupted to replace the acetone. About 60 g. of the extracted gutta-percha was dissolved in 8 liters of toluene to which 0.6 g. of phenyl-2-naphthylamine had been added. The dissolution of the gutta-percha and its subsequent precipitation were conducted in an atmosphere of nitrogen, and the sample was protected from direct light. After the resulting solution was passed through a coarse sintered glass filter, the gutta-percha was reprecipitated by the slow addition of 10 liters of distilled ethanol containing 0.4 g. of phenyl-2-naphthylamine. The precipitate was collected on sintered glass filters, washed with ethanol and dried in vacuo at 35 to 45° for over 30 hours. The gutta-percha purified in this manner was sealed with nitrogen in tubes, each tube containing about 3-5 g. of the sample, and stored at dry-ice temperatures. These latter precautions are necessary, for otherwise rather extensive degradation will occur in a relatively short time. Chemical analyses⁹ show that the gutta-percha purified in this manner contained 98 per cent hydrocarbon, 0.5 per cent acetone-soluble material, 0.05 per cent protein, 0.12 per cent insoluble material and 0.29 per cent ash. The intrinsic viscosity of the polymer in benzene at 30° was 1.14. An extrapolation of the results of Wagner and Flory¹⁰ indicate that the polymer had a viscosity-average molecular weight of about 70,000.

The diluents used in this study, *n*-tetradecane and methyl oleate¹¹, were of technical grade and were used as received. Their densities were measured at two widely different temperatures and a linear variation between these temperatures was assumed. The gutta-percha-diluent mixtures were prepared in a manner identical to that used for the rubber-diluent mixtures in the previous investigation⁴. Compositions were computed at the melting temperatures of the mixtures.

The dilatometric methods¹² previously described in detail were followed in the present work, the dilatometers being immersed in a constant temperature bath regulated to within $\pm 0.1^\circ$. The density of gutta-percha was determined at 0 and 25°, using the method of hydrostatic weighings¹³.

The x-ray diffraction powder patterns were taken with a Geiger counter x-ray diffractometer with Cu K α radiation, operating at 40 kv. and 20 ma. The x-ray diffraction patterns at elevated temperatures were obtained with a camera of the type designed by Mauer and Boltz¹⁴. Temperature control was achieved through the circulation of water from a slowly heated bath set at a predetermined maximum temperature, through the coils originally intended to act as cooling coils for this high temperature camera¹⁴. The temperature of the specimen was recorded by means of an iron-constantan thermocouple placed next to it, and is regarded as accurate to $\pm 0.5^\circ$.

RESULTS AND DISCUSSION

Pure gutta-percha.—Below the melting temperature of the LMF, the crystalline forms observed depend on the previous thermal history of the sample. At

the outset it is important to establish conditions for the formation of each of the modifications so that the properties studied can be properly attributed. If a sample of gutta-percha, after being held at an elevated temperature sufficiently long for all crystallinity to disappear, is rapidly transferred to a thermostat maintained at 0° and left to crystallize isothermally at this temperature, a characteristic x-ray diffraction pattern is obtained (at room temperature) indicated by the dotted lines of Figure 1. The observed Bragg spacings can be identified with β -gutta-percha as defined by Fisher¹⁸, for which an orthorhombic

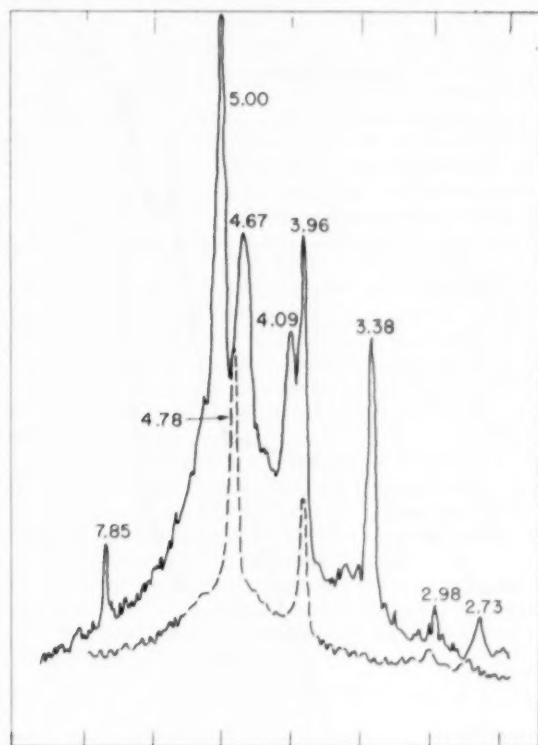


FIG. 1.—X-ray diffraction patterns for two crystalline modifications of gutta-percha at 25°: dotted line is for LMF; solid line, for HMF. Bragg spacings are indicated.

unit cell of dimensions $a = 7.84 \text{ \AA}$, $b = 11.87 \text{ \AA}$, and $c = 4.75 \text{ \AA}$, and a density of 1.04 g./cc. has been proposed. Similarly, if the same sample is crystallized at 55° from the melt, to a pseudoequilibrium value of the degree of crystallinity, then at room temperature the x-ray diffraction pattern indicated by the solid lines of Figure 1 is observed. The Bragg spacings are in agreement with that previously observed for γ -gutta-percha, for which a monoclinic unit cell of dimensions $a = 5.9 \text{ \AA}$, $b = 7.9 \text{ \AA}$, $c = 9.2 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 94^\circ$ and a density of 1.05 g./cc. has been proposed. The patterns in Figure 1 illustrate clearly the fact that at least two different crystal structures can be achieved.

Though the two patterns are quite distinct, the spacings characteristic of the LMF have very similar counterparts in the HMF; the HMF on the other hand has several spacings which are unique to it.

To determine the melting temperatures, T_m^0 , of each of the forms, the dependence of the specific volume on temperature was investigated following the crystallization of a given polymorph. For T_m^0 to be of thermodynamic sig-

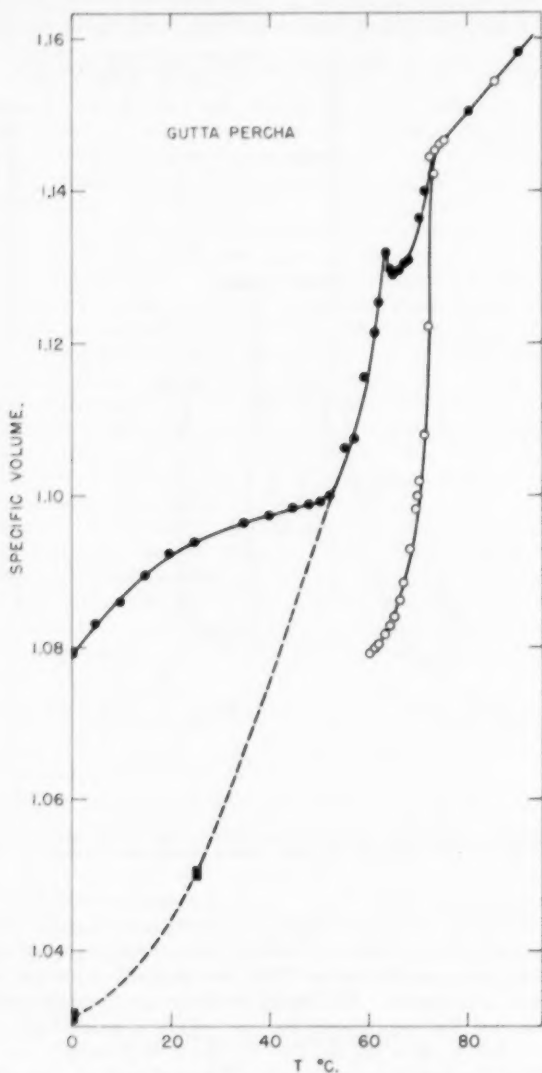


FIG. 2.—Specific volume of gutta-percha as a function of temperature: after crystallization at 0°, ●; after crystallization at 60°, ○; by the method of hydrostatic weighings, ■.

nificance, slow heating rates must be employed to allow for the attainment of a more perfectly crystalline array. Thus up to about 10° below T_m^0 , the temperature was increased in a stepwise manner at a rate of about $1^\circ/12-24$ hrs., while above this temperature the heating rate was decreased to about half this value. At a given temperature the volume increased at first, then decreased, and reached a constant value within the observed time. Behavior of this sort is typical of polymeric systems and has recently been reported for gutta-percha¹⁵. The results of these observations are illustrated in Figure 2, where the final observed specific volumes are plotted against temperature. The open circles represent observations after crystallization from the melt at 60° , crystallization conditions which allow only the formation of the HMF. On subsequent heating the volume followed the path indicated by the open circles, and the melting of this polymorph occurs at 74° . The course of the dilatometric observations after crystallization at 0° , where only the LMF occurs, is indicated by the closed circles of Figure 2. The high volumes observed in the range $0-50^\circ$, and previously reported by Leeper and Schlesinger¹⁵, would appear to be artifacts of the experimental observation, since independent measurements of the specific volume by the method of hydrostatic weighings give values indicated by the solid squares. The dotted curve is thus probably a truer representation of the melting behavior of the LMF. The higher volumes observed dilatometrically could be caused by the fact that the rather rapid crystallization may prevent the mercury from completely penetrating the interior of the sample. This situation will, of course, become alleviated as the temperature is increased. The rather large increase of specific volume is terminated at 64° , where x-ray diffraction patterns indicate the disappearance of spacings attributable to the LMF. This temperature, 64° , is then taken as the melting temperature of the LMF. During the heating process some HMF is developed, and its fusion is indicated by the solid circles in the temperature range $64-74^\circ$. The observed melting temperatures of the respective forms are appreciably higher than some of the values reported in the literature⁶. This is undoubtedly a consequence of the slow heating rates employed in the present investigation; similar behavior has been noted with many other polymers studied.

Polymer-diluent mixtures.—When a low-molecular weight diluent is added to a semicrystalline polymer, its melting temperature is depressed in accordance with the thermodynamic principles of phase equilibria. For polymer-diluent systems it has been shown that¹:

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(V_u/V_1)(v_1 - \chi_1 v_1^2) \quad (1)$$

where T_m is the melting temperature of the polymer-diluent mixture, R the gas constant, ΔH_u the heat of fusion per mole of repeating unit, V_u the molar volume of the repeating unit, V_1 the molar volume of the diluent, v_1 the volume fraction of the diluent and χ_1 is a thermodynamic interaction parameter, which can be written as $\chi_1 = BV_1/RT_m$ where B is the molar free energy change brought about by first neighbor interactions. Equation (1) is analogous to the classical expression for the depression of the freezing point of a liquid. It is applicable to both polymorphs of gutta-percha when the appropriate values of T_m^0 and ΔH_u are used, since the liquid state and thus the thermodynamic interaction parameter are identical in both cases. By rearranging Equation (1), a form more convenient for the analysis of experimental data is obtained. Thus:

$$[1/T_m - 1/T_m^0]/v_1 = (R/\Delta H_u)(V_u/V_1)[1 - (BV_1/R)v_1/T_m] \quad (2)$$

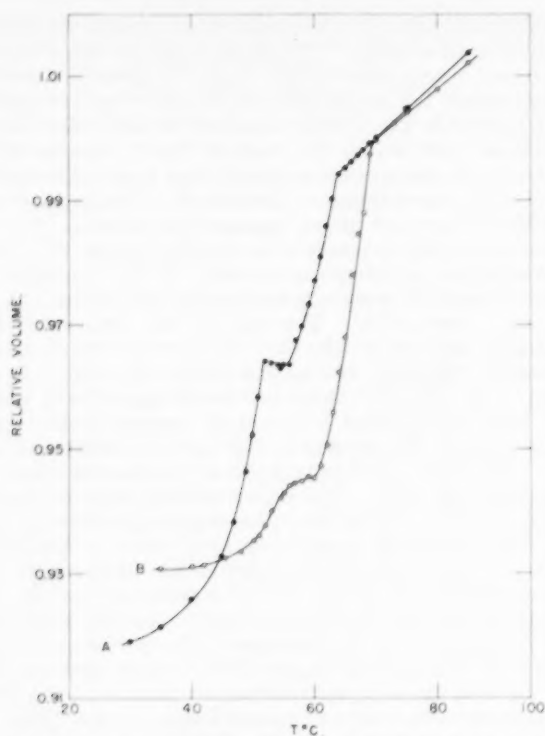


FIG. 3.—Relative volume for gutta-percha-diluent mixtures as a function of temperature: Curve A with tetradecane $v_1 = 0.446$; Curve B with methyl oleate $v_1 = 0.277$.

TABLE I
MELTING TEMPERATURES OF GUTTA-PERCHA-DILUENT MIXTURES

v_1	T_m (HMF) (° C)		T_m (LMF) (° C)	
	Dilatometer	X-ray	Dilatometer	X-ray
With methyl oleate				
0.000	74		64	60-65
0.106	72		59-60	
0.168	71-71.5			56-59
0.266	69.5-70			
0.277	69		56-57	55-58
0.333	68.5-69			55-58
0.422	66-67			53-55
0.573	63.5-64			50-53
With tetradecane				
0.000	74		64	60-65
0.195	69-69.5			
0.195	70	68-70	57.5-58	54-58
0.287	67-67.5		53.5-54	
0.331	66.5-67		53-53.5	53-56
0.446	63.5-64		51-52	51-53
0.570	61.5-62		49-50	44-47
0.696	58.5-59	55-57	45	39-46

Thus, by studying the dependence of the melting temperature of each of the forms on diluent concentration, the respective values of ΔH_u can be obtained, and by making use of the appropriate melting temperatures the free energy of fusion per repeating unit of each of the forms can be calculated.

The melting temperature of the HMF in mixtures with either tetradecane or methyl oleate as diluent can be determined unambiguously by dilatometric means. The heating rates employed were similar to those followed for the bulk polymer, and similar variations of the volume with time under isothermal conditions were observed. Typical results of the volume-temperature behavior of two of the diluent mixtures are given in Figure 3. Curve A is for a mixture containing tetradecane with a volume fraction of 0.446, while Curve B is for a mixture containing methyl oleate, with a volume fraction of 0.277. The melting temperature of the HMF is clearly discernible. The melting temperatures of the HMF of all the mixtures studied are given in Table I and have been plotted according to the method suggested by Equation (2). The plots are well represented by straight lines, the slopes of which are sufficiently close to zero, so that within the experimental error $B = 0$ for either of the diluent mixtures. From the intercepts of these plots ΔH_u is found to be 3145 ± 235 cal./mole of repeating unit, using methyl oleate as diluent, and 2990 ± 110 with tetradecane. The average value of ΔH_u for the HMF is then 3070 ± 130 cal./mole of repeating unit.

The melting temperature of the LMF in the diluent mixtures is not so easily discerned by dilatometric methods. This is due to the fact that the volume change on melting is relatively diffuse and cannot easily be distinguished from the usual recrystallization phenomena that occur. As a consequence of this, the melting temperatures of the LMF were determined by heating the sample in an x-ray diffraction unit and observing the resulting pattern at temperature intervals. The temperature at which the pattern characteristic of the LMF disappeared was taken as the melting temperature. The reliability of the melting point, determined by the x-ray method, was first investigated for the undiluted polymer. In Figure 4 x-ray diffraction patterns of the pure polymer, crystallized under conditions so that only the LMF occurred, were obtained at four different temperatures. From the resulting patterns it can be deduced that melting occurred in the range of 60–65°, which is in excellent agreement with the dilatometric observations. About eight hours elapsed in heating the sample from 50–65°. This is admittedly a rapid heating rate, but apparently in this system sufficient annealing can occur even in this relatively short time. Polymer-diluent mixtures give similar results, as is illustrated in Figure 5, where the diffraction patterns at different temperatures for a gutta-percha-methyl oleate mixture with $v_1 = 0.168$ are given. At 55° the characteristic pattern of the LMF persists, while at 59° it has disappeared. Hence, this mixture has been assigned a T_m of 56–59°. The melting temperatures of the LMF, determined by the x-ray method, are also given in Table I. With the x-ray results as a guide, further examination of the dilatometric data indicated in most cases where the melting occurred. For example, in Figure 3 the gradual rise of volume in the vicinity of 50° and its subsequent leveling off can now be identified with the melting of the LMF.

The rather large uncertainties in the T_m of the LMF in these mixtures precludes a detailed analysis of the data by means of Equations (1) and (2) and hence an accurate determination of ΔH_u for this crystalline form. However, a reasonable estimate of ΔH_u can be obtained. In Figure 6 the melting temperatures of the gutta-percha-methyl oleate mixtures are plotted against composi-

tion. The upper curve, appropriate to the HMF, is calculated from Equation (1), using the parameters just deduced, and the experimental points are indicated by closed circles. The lower three curves are theoretical ones appropriate to the LMF, calculated from Equation (1), using $B = 0$ which is characteristic of the liquid state of the polymer, and values of ΔH_u equal to all of, three-fourths

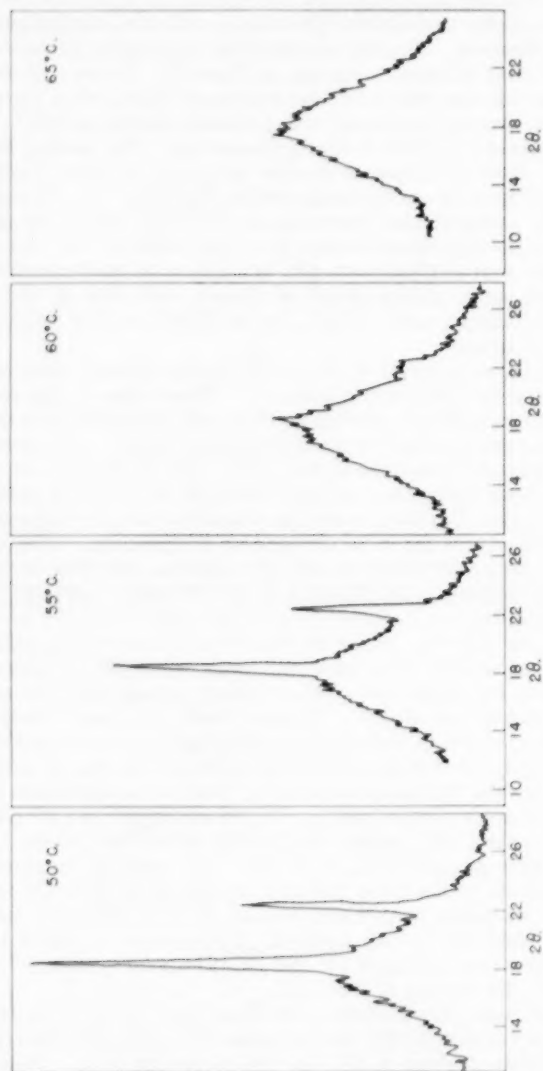


FIG. 4.—X-ray diffraction patterns of the low melting form of pure gutta-percha at various temperatures.

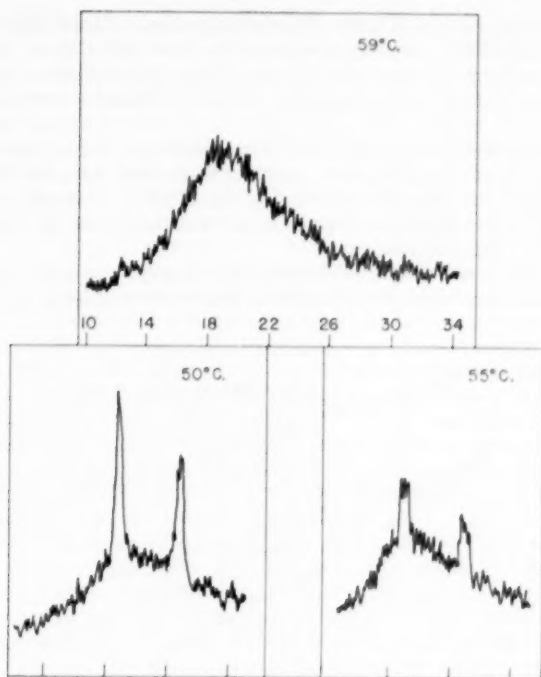


Fig. 5.—X-ray diffraction patterns of the low-melting form of gutta-percha when mixed with methyl oleate $v_1 = 0.168$.

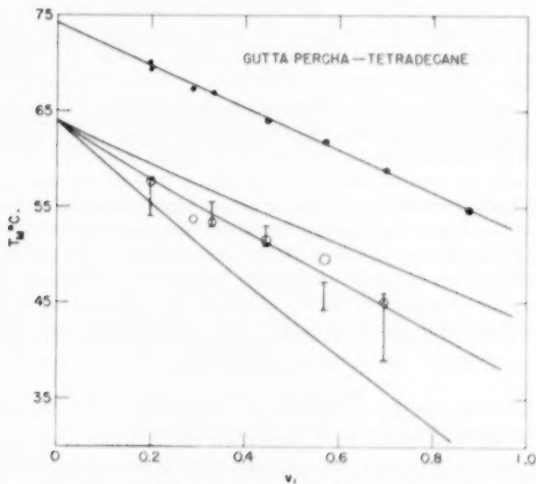


Fig. 6.—Plot of melting temperatures of gutta-percha-methyl oleate mixtures vs. volume fraction of methyl oleate; upper curve for HMF, $\Delta H_s = 3140$ cal./mole; lower three curves for LMF, $\Delta H_s = 3140$, 2356 and 1570 cal./mole, respectively; T_m of HMF, dilatometric method, \bullet ; T_m of LMF, dilatometric method, \circ ; T_m of LMF, x-ray method, \circ .

of and one-half that of the HMF. The melting points of the LMF determined by the x-ray diffraction methods are given by the vertical lines, those by the dilatometric methods, by the open circles. This plot indicates that the ΔH_u appropriate to the LMF is less than that of the HMF and is probably between one-half and three-fourths of it. A similar plot is given in Figure 7 for the data obtained with tetradecane as diluent. The results are concordant with those obtained with methyl oleate, and again indicate that ΔH_u for the LMF is between one-half and three-fourths that of the HMF. This estimation of the ΔH_u for the LMF is adequate enough to allow a discussion of the thermodynamic stability of the two forms.

Thermodynamic parameters.—The stability of polymorphs can be discussed in terms of their respective free energies of fusion per repeating unit. As with

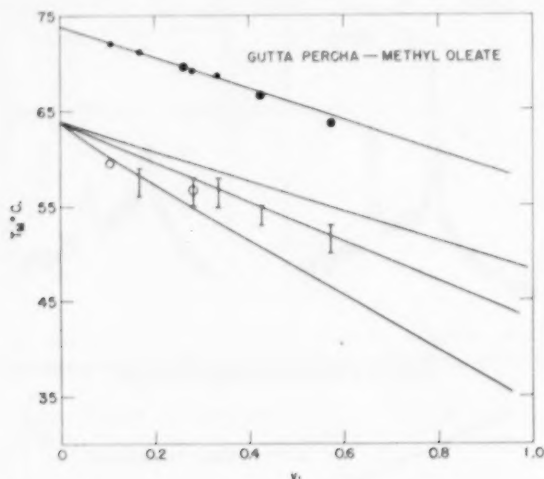


FIG. 7.—Plot of melting temperatures of gutta-percha-tetradecane mixtures vs. volume fraction of tetradecane: upper curve for HMF, $\Delta H_u = 2990$ cal./mole; lower three curves for LMF, $\Delta H_u = 2990$, 2240 and 1495 cal./mole, respectively; T_m of HMF, dilatometric method, \bullet ; T_m of LMF, dilatometric method, \circ ; T_m of LMF, x-ray method, \circ .

polymorphs of low molecular weight crystals at a given temperature, the crystal form which has the lower free energy (relative to a standard state) is the more stable one. Taking the completely liquid polymer as our standard state, the crystalline modification having the greater free energy of fusion per repeating unit should be the more stable one. Thus, if at a temperature T below its melting temperature, the LMF should be the more stable one, then:

$$\Delta f_u^{\text{LMF}} > \Delta f_u^{\text{HMF}} \quad (3)$$

where Δf_u is the free energy of fusion per repeating unit. Since $\Delta f_u = \Delta H_u (1 - T/T_m^0)$ the condition for stability would be that:

$$\Delta H_u^{\text{LMF}} > \Delta H_u^{\text{HMF}} [(1 - T/T_m^{0\text{HMF}}) / (1 - T/T_m^{0\text{LMF}})] \quad (4)$$

Since $T_m^{0\text{HMF}} > T_m^{0\text{LMF}}$, a minimum requirement for the stability of the LMF is that its heat of fusion per repeating unit be greater than that of HMF. Al-

though ΔH_u^{LMF} could not be determined precisely, as was already mentioned, it was found nevertheless to be appreciably less than ΔH_u^{HMF} . It is, therefore, concluded that the LMF is a metastable modification in the temperature interval studied, in agreement with the earlier surmises¹⁷ based solely on kinetic observations¹⁸.

It thus appears that the thermodynamics of the polymorphism in semi-crystalline polymers can be described in a manner similar to the methods used for low molecular weight materials. A third polymorph of gutta-percha, predicted by Fuller⁸ and by Bunn¹⁹ and recently discovered by Fisher⁶, occurs only when the sample is stretched. The stretching process increases the free energy of the pure liquid and thus, under these conditions, this modification may become thermodynamically favored. Alternatively, prior to deformation this modification may be thermodynamically favored, the deformation process only serving to favor its crystallization kinetics. This question must remain unresolved until the free energy of fusion of this form is evaluated.

The heat of fusion of the HMF is appreciably greater than that of natural rubber, the *cis*-polyisoprene for which a value of 1050 cal./mole has been reported⁴. For low-molecular weight hydrocarbons, the heats of fusion for the isomers in the *trans*-configuration are greater than those for the *cis*-configuration. However, the differences in the heat of fusion of the two low molecular weight isomers are not so great as is observed here for the two polymeric hydrocarbons. A possible reason for the large difference in ΔH_u may reside in the crystal structures of natural rubber and the HMF of gutta-percha. According to Bunn¹⁹ the unit cell of natural rubber has four chains passing through it, but two are right-handed chains and two are left-handed chains. On the other hand, the unit cell of gutta-percha is composed entirely of either right- or left-handed molecules. Thus, the greater asymmetry of the long-chain *cis*-hydrocarbon and its effect in the packing of the crystal might contribute to its lower heat of fusion.

The entropy of fusion of the HMF is calculated to be 8.8 cal./deg./repeating unit or 2.93 cal./deg./single bond. For the LMF the entropy of fusion is calculated to be 7.0 cal./deg./repeating unit or 2.34 cal./deg./single bond. These are appreciably larger than for natural rubber⁴ where the entropies of fusion for the single crystal form observed are 3.46 cal./deg./repeating unit and 1.15 cal./deg./single bond, respectively, and for other polymers² where the entropy of fusion per single bond has been found to be in the order of R .

Although it has been tacitly assumed that the major contribution to the entropy of fusion is the configurational freedom gained by the chain units in the liquid state, it is also necessary to consider the entropy change which arises from the volume increase which occurs on melting. This contribution to the entropy of fusion can be calculated²⁰ from the well known relation:

$$(\partial S / \partial V)_T = -\alpha / \beta \quad (5)$$

where α is the volume-temperature coefficient at constant pressure and β is the volume-pressure coefficient at constant temperature. Thus:

$$\Delta S_v = -(\alpha / \beta) \Delta V_u \quad (6)$$

where ΔS_v is that portion of the entropy change per repeating unit due to ΔV_u , the volume increase per repeating unit on melting; α and β are evaluated for either the crystalline or liquid phases at the melting point. The entropy of fusion, ΔS_u , can be considered to be approximately the sum of ΔS_e and ΔS_v , where ΔS_e is the increase in configurational entropy on fusion. To evaluate

ΔS_v , the volume-temperature coefficient, the volume-pressure coefficient, and the specific volumes of the liquid and the all-crystalline polymer at the melting temperature must be known. For amorphous natural rubber at its melting temperature $\alpha = 7.42 \times 10^{-4} \text{ cm}^3/\text{g./deg.}^{21}$, $\beta = 60 \times 10^{-6} \text{ cm}^3/\text{g./bar}^{22}$ and $\Delta V_u = 0.098 \text{ cm}^3/\text{g.}^{23}$ so that $\Delta S_v = 1.8 \text{ cal./deg./mole of repeating unit}$, which is an appreciable portion of the observed ΔS_u . The gain of the configurational entropy on fusion is, then, $1.7 \text{ cal./deg./mole of repeating unit}$. Not all the quantities entering Equation (6) are known for gutta-percha so only an approximate calculation can be made for ΔS_v . Taking 1.05 g./cc. as the density of the unit cell of the HMF at 20° and assuming that its volume-temperature coefficient is $2 \times 10^{-4} \text{ cm}^3/\text{g./deg.}$, one finds ΔV_u at 74° to be $0.182 \text{ cm}^3/\text{g. of repeating unit}$. From the data in Figure 2, the volume-temperature coefficient of the amorphous gutta-percha is $7.5 \times 10^{-5} \text{ cm}^3/\text{g./deg.}$, and we assume that the volume-pressure coefficient at 74° is $60 \times 10^{-6} \text{ cm}^3/\text{g./bar}$, the same as for natural rubber. Since the volume-pressure coefficient of amorphous gutta-percha has not been measured, the calculated value of ΔS_v will be in error because of uncertainty in the value assumed. From Equation (6) ΔS_v for the HMF of gutta-percha is then $3.7 \text{ cal./mole/deg.}$, giving $5.1 \text{ cal./mole/deg.}$ for the configurational contribution to the entropy of fusion. Thus the volume change on melting makes a significant contribution to the observed entropy of fusion both for natural rubber and gutta-percha and presumably for other semicrystalline polymers as well. In fact, similar contributions have been observed in metals²⁴ and more recently in low-molecular weight hydrocarbons²⁵, so they appear to be quite general.

The configurational entropy change per HMF unit of gutta-percha is still about three times that of natural rubber at their respective melting temperatures. According to the lattice treatment of polymer configurations²⁶ the entropy of disorientation per mole of segments at constant volume is given by:

$$\Delta S = R \ln [(Z - 1)/e] \quad (7)$$

where Z is the lattice coordination number. A segment is defined as the size of a unit in the corresponding freely jointed chain. This is a chain which matches the contour length and the unperturbed root-mean-square displacement length of the actual chain molecule. Unfortunately, from the experimentally determined ΔS_u we calculate the disorientation entropy per repeating unit so a direct comparison with Equation (7) cannot be made. However, from Equation (7) we can expect that the disorientation entropy should be greater for the more flexible chain, and for a chain having a higher value of Z , that is, the more disordered the packing in the liquid state. Thus, if the packing in the liquid state is the same for both rubber and gutta-percha, the results for the configurational entropy of fusion indicate that the gutta-percha molecule is more flexible in the liquid state. Conversely, if the two chain molecules possessed the same flexibility, the liquid packing in gutta-percha would appear to be the more disordered. According to Wall's²⁷ calculations a freely rotating gutta-percha molecule, wherein the normal bond distances and valence angles are maintained, will have a greater extension in space than the corresponding rubber molecules. However, the investigations of Wagner and Flory¹⁰ indicate that, in the unperturbed state, i.e., in the absence of the effect of solvent, the natural-rubber molecule has a greater extension relative to its size calculated by assuming free rotation. They find that the values of the ratio of the unperturbed end-to-end distance to that for free rotation are 1.71 and 1.46 for

natural rubber and gutta-percha, respectively. Thus steric effects and the potentials hindering rotation about the single bonds are obviously different in the two cases and allow the molecule in the *trans*-configuration to be the more compact one. The greater flexibility of gutta-percha in the liquid state would then contribute to the larger value observed for the change in configurational entropy on melting.

Crystallization kinetics.—When a sample of gutta-percha is brought from a temperature above the melting temperature of the HMF to any temperature below, crystallinity develops in a well-defined reproducible manner when care is taken to start with a completely melted sample. The isotherms which result when the specific volume is plotted against time display the characteristic sigmoidal shape that has been observed for a wide variety of polymer systems²⁸. In the temperature range of 20–60°, the isotherms at the various temperatures are superposable merely by rescaling the time, which again is in agreement with observations on many polymers²⁹. The rate of crystallization depends very strongly on the temperature, as is indicated in Table II, where τ_i , the time at which crystallinity is first observed, is given at various temperatures. τ_i depends on the over-all crystallization rate, i.e., the nucleation and growth rates

TABLE II
TIME FOR DETECTION OF CRYSTALLINITY AT VARIOUS
CRYSTALLIZATION TEMPERATURES

T (° C)	τ_i (min.)	T (° C)	τ_i (min.)
0	<3	51	60
20	<3	53	80
35	3–5	55	160
40	7–10	57	340
45	20	59	500–1700
49	43		

as well as the sensitivity of the crystallinity detector. Thus its variation with temperature can be taken as a relative measure of the temperature coefficient of the crystallization rate constant.

An examination of the data in Table II as well as the isotherms indicates that the crystallization rate constant is a smoothly varying function of temperature, despite the fact that x-ray diffraction analysis indicates that at different temperatures different polymorphs are occurring. For example, when crystallinity develops from the melt at 55° and higher temperatures, only the HMF occurs; at 50 and 40°, both the HMF and LMF form; while below 40°, only the LMF occurs. One concludes, therefore, that the crystallization rate is independent of the form of the polymorph which results.

SUMMARY

The melting temperatures of two of the crystalline modifications of gutta-percha and their mixtures with either methyl oleate or tetradecane as diluent were determined by x-ray diffraction and dilatometric methods. It was found that the melting temperatures of the two forms in the pure polymer were 64 and 74°, respectively. From these studies the heat of fusion per repeating unit of the high melting form was deduced to be 3070 ± 250 cal./mole, while the heat of fusion for the low melting modification was found to be about one-half to three-fourths this value. An analysis indicates the low melting form is a metastable one. The heats and entropies of fusion of each of the forms of

gutta-percha are appreciably greater than those of the monomorphic *cis*-hydrocarbon, natural rubber. The difference in the entropies of fusion of the two polymers persists even when allowance is made for the significant contribution of the volume change accompanying fusion.

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CRYSTALLIZATION AND THE RELAXATION OF STRESS IN STRETCHED UNVULCANIZED NATURAL RUBBER *

A. V. TOBOLSKY AND G. M. BROWN

FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY,
PRINCETON, NEW JERSEY

The first observation made in this laboratory in 1946 on the effect of crystallization on stress decay at constant extension was made on a vulcanized Neoprene GN gum stock¹. It was found that this rubber showed only slight stress decay after 100 hours at 35° C and 50 per cent extension. However, a complete decay of stress to zero stress was observed after only 50 hours at 0° C and 50 per cent extension. Furthermore, the sample after reaching zero stress began to increase in length (spontaneous elongation). This phenomenon was attributed to crystallization. Observations of spontaneous elongation, but no stress decay measurements, were previously reported for vulcanized and unvulcanized natural rubber and for vulcanized and unvulcanized ether polysulfide rubber².

It was decided to make a careful study of the effect of temperature and elongation on the stress-decay curves of unvulcanized rubber (cast latex sheet³) in the temperature region of crystallization. Some time after these studies were completed⁴, two papers have appeared in which stress decay to zero stress in rubber vulcanizates due to crystallization were reported⁵. In one of these a rather thorough study was made of the decay of stress and change in volume of a natural rubber vulcanizate at -26° C and maintained at four different extension ratios⁶. Our own work on unvulcanized natural rubber was carried out at seven different temperatures in the crystallization region, and were made at five different extension ratios. Quite surprisingly, four of these are the same as were used by Gent⁶. There are interesting differences as well as similarities between our work and the results reported for vulcanized natural rubber.

EXPERIMENTAL RESULTS

The experimental methods used for measurement of stress relaxation were described previously⁷. Experiments were performed at several temperatures for elongations of 50 and 150 per cent, and at various elongations for temperature of 0 and -20° C.

The results are shown in Figures 1-4. The ordinate is g_{25} , which is defined as the stress in lb. per sq. in. times $298/T$, where T is the absolute temperature. The abscissa is the logarithm of the time (in hours).

In Figure 1 the stress decay curves are shown for samples maintained at 50 per cent elongation (extension ratio 1.5) at temperatures of 0°, -10°, -20°, -25°, -30°, -40°, and -50° C. In Figure 2 the stress decay curves are shown for samples maintained at 150 per cent elongation (extension ratio 2.5) at temperatures of 0°, -15°, -20°, -25°, and -40° C. Taking the time required to attain zero stress as an index of the rate of crystallization, it is clear

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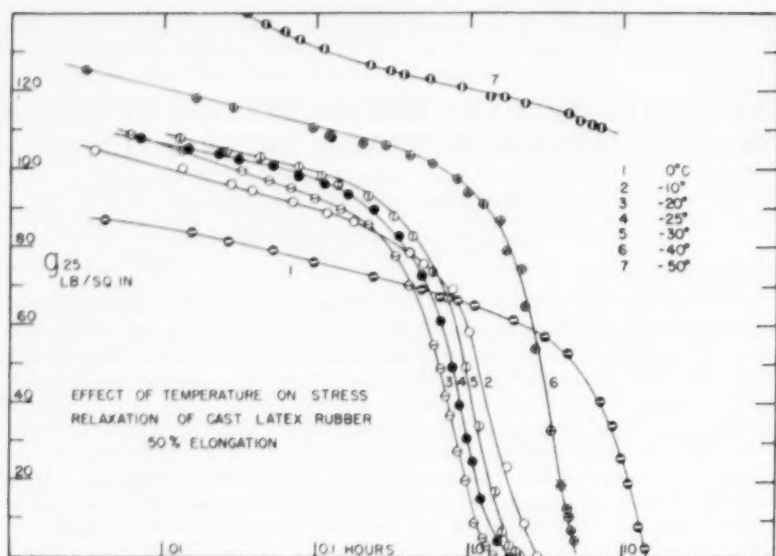


FIG. 1.

that the results of Figures 1 and 2 are in qualitative accord with the results of Bekkedahl, who studied the rates of crystallization in unvulcanized natural rubber (unstretched) by a dilatometric procedure.⁸ Bekkedahl found that there is a maximum rate of crystallization for unstretched natural rubber at

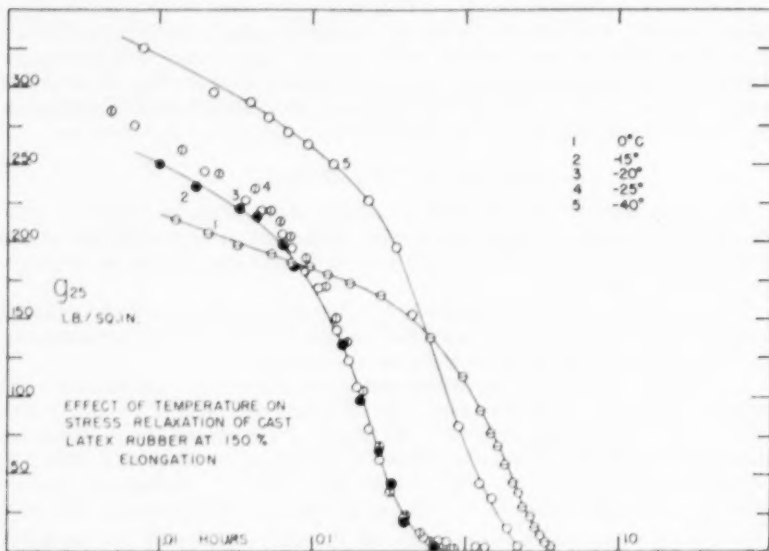


FIG. 2.

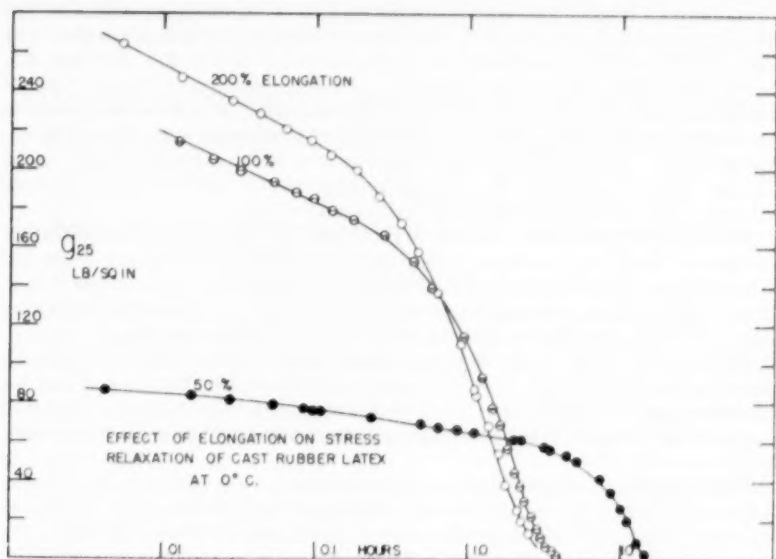


Fig. 3.

-25° C. We find that the maximum rate of stress decay at a 1.5 extension ratio occurs at -20° C. At an extension ratio of 2.5, the rate of stress decay is less sensitive to temperature, with a flat maximum in the neighborhood of -20° C. At -50° C the rate of crystallization is very slow.

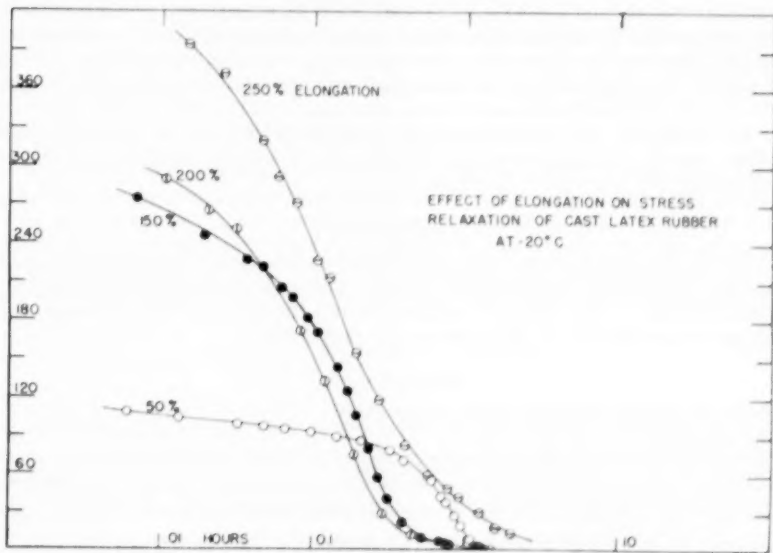


Fig. 4.

In Figure 3 stress decay curves are shown at 0° C for samples maintained at extension ratios 1.5, 2.0, and 3.0. In Figure 4 stress decay curves are shown at -20° C for samples maintained at extension ratios of 1.5, 2.5, 3.0, and 3.5. Gent's stress decay curves are shown for vulcanized natural rubber at -26° C maintained at extension ratios of 1.5, 2.0, 2.5, and 3.0. It is interesting to note that Gent concluded that the rate of stress decay increases with increasing extension ratio. Our work indicates that this is true for extension ratios up to 3.0, but Figure 4 indicates that the decay of stress at -20° C is slower at an extension ratio of 3.5 than at an extension ratio of 3.0.

At the higher extension ratios it is probable that the rate of crystallization becomes so rapid that a large portion of the crystallization occurs while the sample is being stretched and therefore does not contribute to the stress decay. Indeed, at the higher elongations there was always a very noticeable whitening of the originally translucent samples while they were being stretched.

The time for decay of stress to zero stress found in these studies for unvulcanized natural rubber at -25° C was very much faster than that found for vulcanized natural rubber at -26° C at the same extension ratios. This is, of course, to be expected, since crosslinking is known to interfere with the crystallization process.

After certain of the stress decay experiments were completed, the melting of the crystals was studied by following the recovery of stress in the samples as the box was heated to room temperature. As the temperature was raised, the stress kept increasing as the crystals melted out until, at a certain temperature, a maximum value of stress was reached. Above this temperature, the stress began to decrease again because of molecular flow of this noncrosslinked polymer. This maximum in stress occurred at a fairly sharply defined temperature which should correlate fairly well with the upper melting temperature T_m . In the present experiments at a relative extension of 1.5, the values of T_m obtained in this approximate way are about +2°, -3°, +2°, and +6° C for relaxation temperatures of -40°, -25°, -20°, and -10° C, respectively. These results are very similar indeed to those found by Bekkedahl and Wood². Increasing the relative extension appears to increase the upper melting temperature. Thus at a relative extension of 2.5 the upper melting temperatures that we found were 10°, 5°, 10°, and 12° for relaxation temperatures of -40°, -25°, -20°, and 0° C.

In conclusion, the measurement of stress decay at constant extension does indeed provide a sensitive method for following the crystallization of both unvulcanized and vulcanized polymers.

SYNOPSIS

Decay of stress to zero stress followed by spontaneous elongation occurs in samples of stretched unvulcanized natural rubber in the temperature region of crystallization. Experimental results showing the effect of temperature and elongation on the rate of stress decay are presented.

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VISCOELASTIC BEHAVIOR OF POLYISOBUTYLENE UNDER CONSTANT RATES OF ELONGATION *

THOR L. SMITH

JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA

INTRODUCTION

A variety of methods has been used to study the viscoelastic properties of polymeric materials. These methods include the response to sinusoidal stress (dynamic measurements¹), stress relaxation², and creep under constant load³ and constant stress⁴. The present investigation was made to determine whether or not the viscoelastic properties of rubberlike materials over an extended time scale could be obtained from stress-strain curves measured at different strain rates and temperatures.

Polyisobutylene of high molecular weight was selected for study, since its viscoelastic properties have been investigated extensively in a cooperative program sponsored by the National Bureau of Standards. From the data obtained, Marvin⁵ has derived the distribution functions of relaxation and of retardation times over a time scale of 10^{-10} to 10^7 sec. These functions show quantitatively a change in properties from liquidlike to rubberlike to glasslike with decreasing time scale.

The equilibrium stress-strain curves for lightly crosslinked rubber and other elastomers are closely linear for elongations up to 100 per cent⁶. The non-equilibrium (viscoelastic) stress-strain curves for similar and noncrosslinked elastomers might be expected to be linear viscoelastic, as a first approximation, at temperatures above the glass transition, provided the strain and the strain rate are not excessively large. Nonlinear viscoelastic effects are usually pronounced for materials in their glasslike state and at large strains.

THEORETICAL DISCUSSION

The viscoelastic properties of a material when subjected to a constant rate of deformation have been discussed briefly by Alfrey⁷ and by Sips⁸. The stress-strain curves can be related conveniently to a generalized Maxwell model (an infinite number of Maxwell elements connected in parallel) as is usually done for stress-relaxation and dynamic data. If a Maxwell model is subject at zero time to a constant rate of strain R , the stress-strain curve is given by the equation:

$$S/R = \int_{-\infty}^{\infty} M(\tau) \tau (1 - e^{-\gamma/R\tau}) d \ln \tau \quad (1)$$

where S is the stress, γ the strain, and $M(\tau)$ the relaxation distribution function which is defined such that $M(\tau) d \ln \tau$ is the contribution to the instantaneous tensile modulus of those elastic mechanisms whose relaxation times lie between $\ln \tau$ and $\ln \tau + d \ln \tau$. Equation (1) states that S/R is a function only of γ/R . Thus, data obtained at different strain rates should superpose to give a

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single curve on a plot of $\log S/R$ vs. $\log \gamma/R$. Data obtained at different temperatures can be combined by using Ferry's reduced-variable scheme⁹, which is based on the assumptions that all relaxation times have the same temperature dependence and that the modulus of each spring in the model is proportional to the absolute temperature. By introducing these assumptions, Equation (1) becomes:

$$ST_0/RTa_T = \int_{-\infty}^{\infty} M(\tau)\tau(1 - e^{-\gamma/Ra_T\tau})d \ln \tau \quad (2)$$

where T_0 is an arbitrary reference absolute temperature, T the temperature at which S and γ are measured, and a_T the ratio of any relaxation time at T to its value at T_0 . Thus, data measured at different temperatures and strain rates should superpose on a plot of $\log ST_0/RTa_T$ vs. $\log \gamma/Ra_T$. The quantities ST_0/RTa_T and γ/Ra_T will be termed reduced stress S_r and reduced strain γ_r . Thus, a plot of S_r vs. γ_r is a hypothetical stress-strain curve measured at unit strain rate and at temperature T_0 .

The quantity a_T can be determined from stress-strain data measured at various temperatures. Graphs are made of $\log ST_0/RT$ vs. $\log \gamma/R$, and the curves for different temperatures are shifted along a line of unit slope until they superpose. $\log a_T$ as a function of temperature is calculated from the magnitudes of the shifts. A similar method has been used to superpose dynamic viscosity data¹⁰. For noncrosslinked materials, a_T can be calculated from the temperature dependence of the steady-flow viscosity⁹, since:

$$a_T = \eta T_0/\eta_0 T$$

where η and η_0 are the viscosities at T and T_0 , respectively.

The stress-relaxation modulus $E_r(t)$ can be derived readily from a plot of $\log S_r$ vs. $\log \gamma_r$. By differentiating Equation (2) with respect to reduced strain, the following equation for $E_r(t)$ is obtained:

$$dS_r/d\gamma_r = \int_{-\infty}^{\infty} M(\tau)e^{-t/\tau}d \ln \tau \equiv E_r(t) \quad (3)$$

where γ/Ra_T has been replaced by reduced time t since the two are equivalent by definition. For computational purposes, the following equivalent equation is convenient:

$$E_r(t) = (S_r/\gamma_r)(d \log S_r/d \log \gamma_r) \quad (4)$$

After $E_r(t)$ has been obtained, $M(\tau)$ can be calculated by using various approximation methods that have been described and used previously^{5,11}.

The stress-strain curve predicted by Equation (1) for a typical noncrosslinked material is shown in Figure 1. On a log-log plot, the curve has four characteristic portions: (1) at small values of γ_r , the slope is essentially unity, and the material exhibits a glasslike modulus, about $10^{10.5}$ dynes/cm²; (2) at somewhat larger values of γ_r , the slope is less than unity and gives a qualitative indication of the relative magnitudes of the viscous and elastic forces, e.g., a zero slope on a plot of $\log S$ vs. $\log \gamma$ results when only viscous forces are operative, and a unit slope, when only elastic forces are present; (3) at intermediate values of γ_r , the slope is only slightly less than unity, and the material exhibits a rubberlike modulus, about 10^7 dynes/cm²; (4) at large values of γ_r , the slope is zero, and only viscous flow occurs. With crosslinked materials, the last

portion is not observed since a permanent deformation or ordinary viscous flow cannot take place.

At a single temperature and strain rate, it is possible to measure only some segment of the reduced stress-strain curve because of limitations in experimental methods. In order to measure directly the entire curve at a single temperature, it would be necessary to vary the strain rate by a factor of about 10^{15} . The upper limit of strain rate that can be used is set by the velocity of propagation of the stress wave and the dimensions of a specimen and is in the range of 10^2 to 10^3 sec.⁻¹. The lower limit is determined only by what is experimentally practical and, thus, is in the range of 10^{-6} sec.⁻¹. Hence, it should be possible to measure at a single temperature a sizable portion of the entire stress-strain curve.

Equation (1) would not be expected to apply to real materials at temperatures below their glass transition (except possibly for infinitesimally small strains) due to pronounced nonlinear viscoelastic effects. The reduced-variable treatment as applied in Equation (2) appears to break down for materials at temperatures near their glass transition. This breakdown may be due to non-

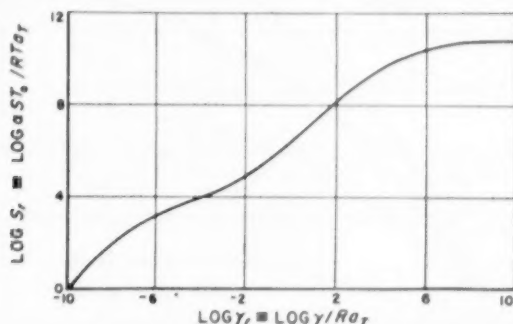


Fig. 1.—Stress-strain curve at unit strain rate for a typical linear viscoelastic material.

linear effects and also to the fact that the assumptions of the reduced-variable scheme, in the form used, are not valid¹². However, Philippoff¹³ has made dynamic measurements at temperatures both above and below the glass transition and reports that the reduced-variable scheme (at least for the small strains used) is valid over the entire temperature range.

EXPERIMENTAL PROCEDURE AND MATERIAL

The polyisobutylene studied was part of the material used in the cooperative research program sponsored by the National Bureau of Standards. The molecular weights⁵ as obtained by intrinsic viscosity and light scattering are: $\bar{M}_v = 1.35 \times 10^6$ and $\bar{M}_w = 1.56 \times 10^6$. The temperature dependence of the steady-flow viscosity from which values of a_T were calculated is given by the equation⁷:

$$\log \frac{\eta}{\eta_0} = 0.504 \times 10^6 \left(\frac{1}{T^2} - \frac{1}{T_0^2} \right) \quad (5)$$

The material was pressed into sheets about 0.10 inch in thickness, care being taken to remove all air bubbles during the operations. Dumbbell-shaped tensile specimens with a gage length of 2.25 inches and a width of 0.50

inch were die-cut from the sheets. Tensile data were measured with an Instron tensile tester at crosshead speeds of 0.02 to 20.0 in./min. and at ten temperatures between -54 and 85°C . The specimens were clamped in the Instron by compression jaws set, initially, 3.0 inches apart. Temperature was controlled by an air thermostat placed around the compression jaws of the Instron.

The recorder of the Instron gives a plot of force vs. time; the time axis is directly proportional to crosshead displacement. From the recorded force, the stress was calculated on the basis of the initial cross-sectional area of the specimen and was then converted to stress based on the actual cross section, as described below. The strain in a specimen was calculated from the crosshead displacement, using an effective gage length of 3.2 inches. This value for the

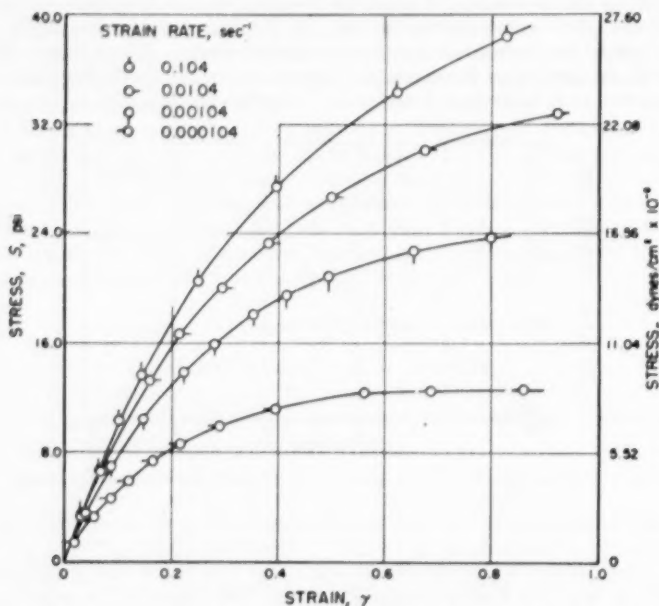


Fig. 2.—Dependence of stress-strain curve on strain rate at 26.7°C . Stress calculated on basis of original cross-sectional area.

effective gage length was determined by a photographic method in a separate study⁶, which showed: (1) that the strain in the uniform portion of a specimen can be calculated from crosshead displacement, using an effective gage length of 3.2 inches, and (2) that this gage length is essentially constant for elongations up to 150 per cent. At greater elongations, the effective gage length increases because the specimen exudes from the compression jaws. It was thus concluded: (1) that reliable strain data could be obtained without the direct use of an extensometer and (2) that a constant cross head speed imposes a constant strain rate for elongations up to about 150 per cent.

EXPERIMENTAL RESULTS AND DISCUSSION

The equilibrium stress-strain curve for lightly vulcanized rubber is linear for extensions up to 100 per cent only if the stress is calculated on the basis of

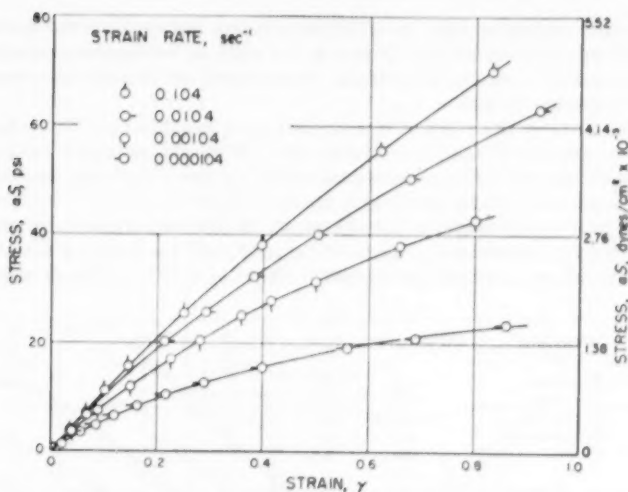


FIG. 3.—Data of Figure 2, except stress (αS) calculated on basis of actual cross-sectional area.

the actual cross-sectional area of a specimen. It follows that Equations (1) and (2) can be expected to hold for large values of γ only if the stress is calculated in this manner. Stress calculated on the basis of the original cross-section can be converted into stress based on the actual cross-section by multiplying by

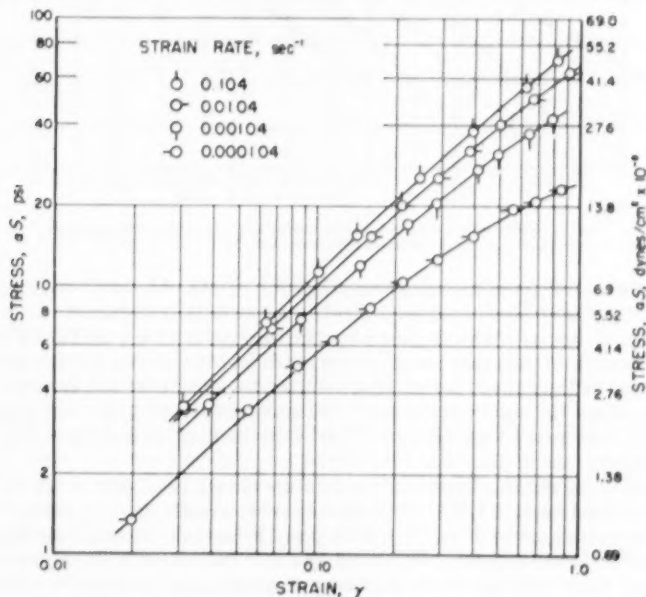


FIG. 4.—Data of Figure 3 on double logarithmic plot.

the principal extension ratio α . This conversion is based on the assumption that Poisson's ratio is 0.5, which is true for unfilled rubberlike materials. In the discussion of experimental results, stress based on the actual cross-section will be designated by αS .

Figure 2 shows the effect of strain rate on S - γ curves at 26.7°C. In Figure 3 the same data are plotted as αS vs. γ , and in Figure 4, as $\log \alpha S$ vs. $\log \gamma$. It is seen that the curves depend considerably on the strain rate and that less curvature occurs on a plot of αS vs. γ than on a plot of S vs. γ .

To show that stress-strain data obtained at different strain rates superpose as predicted by Equation (1), plots of $\log \alpha S T_0 / RT$ vs. $\log \gamma / R$ are shown in Figure 5 for data at five temperatures. (The $\log \gamma / R$ coordinate was shifted

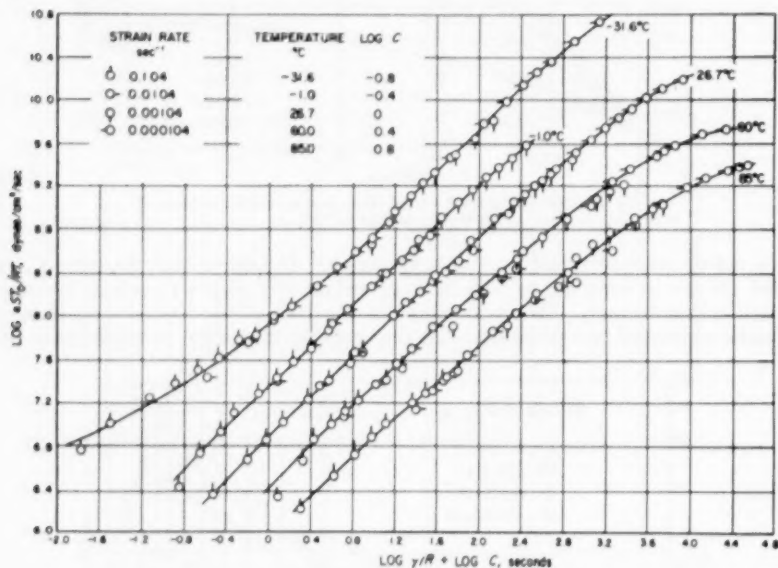


Fig. 5.—Stress-strain data reduced to unit strain rate at five temperatures between -31.6 and 85°C.

the amount $\log C$ for convenience in display.) Data obtained for elongations up to 100 per cent are shown, and good superposition is obtained.

Values of $\log a_T$ were obtained by shifting plots of $\log \alpha S T_0 / RT$ vs. $\log \gamma / R$ along a line of unit slope until curves for different temperatures superposed. The distances the curves are shifted, relative to a curve at the standard temperature, equal the values of $\log a_T$. The standard temperature was first taken as 26.7°C and was changed later to 25.0°C by making a small correction to all $\log a_T$ values.

Values of a_T obtained by shifting data are shown in Figure 6, where $\log a_T T / T_0$ is plotted against $1/T^2$. It is seen that the results are in good agreement with values obtained by Ferry, Grandine, and Fitzgerald from the superposition of dynamic-viscosity data¹. The solid line was calculated from Equation (5), which has been obtained from viscosity measurements. Since Marvin⁶ used values of a_T calculated from Equation (5) to combine data obtained in the co-

operative research program, the same values were used to construct the reduced stress-strain curve, shown in Figure 7, instead of a_T values obtained from data superposition. Only data obtained at elongations less than 100 per cent are shown in Figure 7. At large values of $\log \gamma_r$, $\log S_r$ is shown to equal 11.3, since this is the value for Trouton's coefficient of viscous traction at 25° C, which equals three times the Newtonian viscosity¹. All data superpose on the reduced plot satisfactorily except the data obtained at the lowest temperatures, near the glass transition (-71° C), where Equation (2) may not be applicable.

Although polyisobutylene shows marked non-Newtonian flow behavior, these so-called non-Newtonian properties should not affect the superposition of the data in Figure 7. The reduced stress is defined in the same way as is

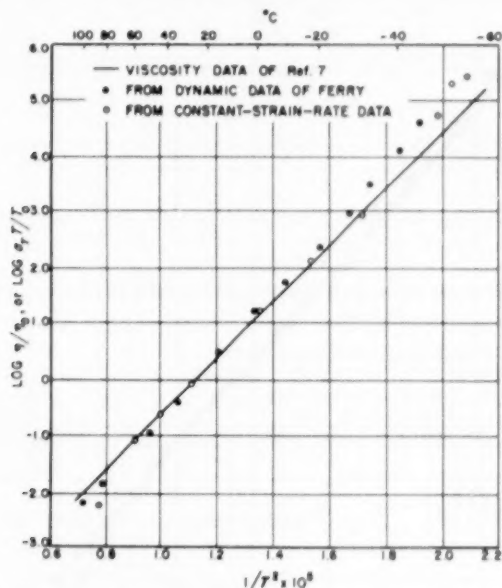


Fig. 6.—Temperature dependence of $a_T T/T_0$ plotted logarithmically against $1/\dot{\gamma}$.

apparent viscosity η_a , i.e., stress divided by strain rate R , and the reduced strain has dimensions of time (the reciprocal of the dimensions of strain rate). Thus, the plot in Figure 7 is formally the same as a plot of $\log \eta_a$ vs. $-\log R$, which shows the dependence of η_a on strain rate. The reduced stress differs, however, from apparent viscosity in that reduced stress refers to a nonequilibrium state while apparent viscosity refers to a steady-state condition. Padden and De Witt¹⁴ have found that the reduced-variable scheme can be applied to apparent viscosity data, measured at different strain rates and temperatures, in a manner similar to that used in superposing stress-strain data. Philippoff¹⁵ has found that the curve of $\log \eta_a$ vs. $\log R$ for a 20 per cent solution of polyisobutylene in decalin is similar in shape to a log-log plot of dynamic viscosity η' vs. frequency ω . At low frequencies and strain rates the two curves superpose, but at high frequencies and strain rates the dynamic viscosity decreases faster than does the steady-flow viscosity. (A recent theory by De Witt¹⁶ predicts that the

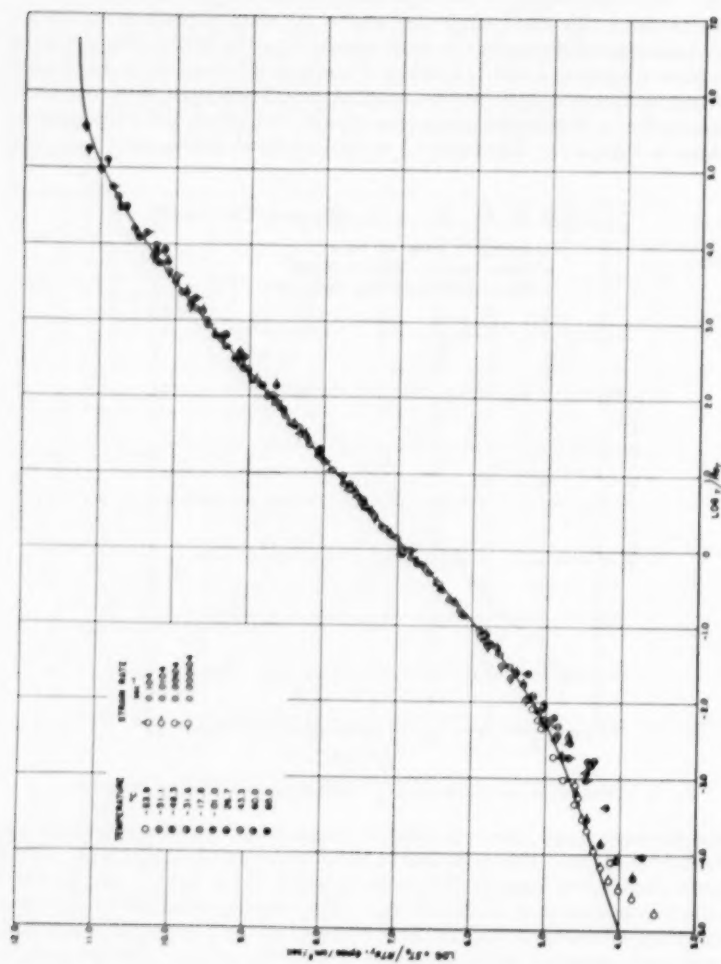


FIG. 7.—Stress-strain data reduced to unit strain rate and 298° K. Data obtained at strain rates between 0.104 and 0.104×10^{-4} sec.⁻¹ and ten temperatures between -53.9 and 85° C.

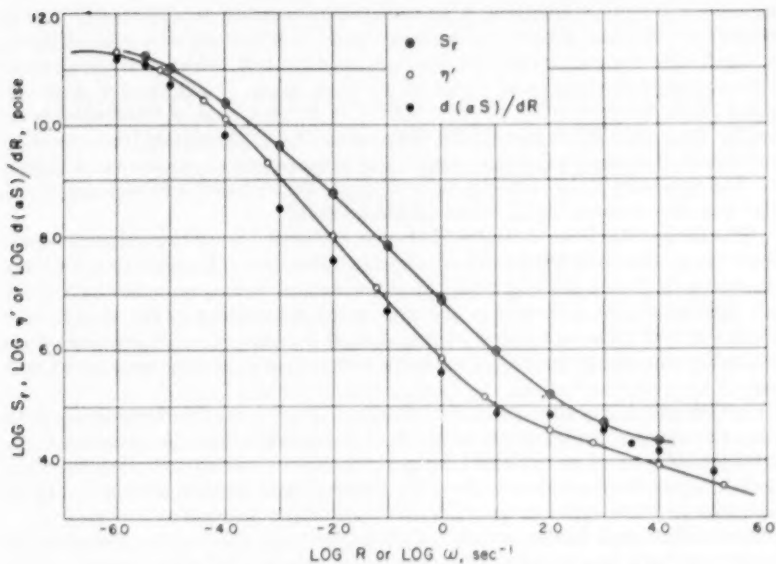


FIG. 8.—The time dependence of dynamic viscosity η' , S_r , and $d(aS)/dR$.

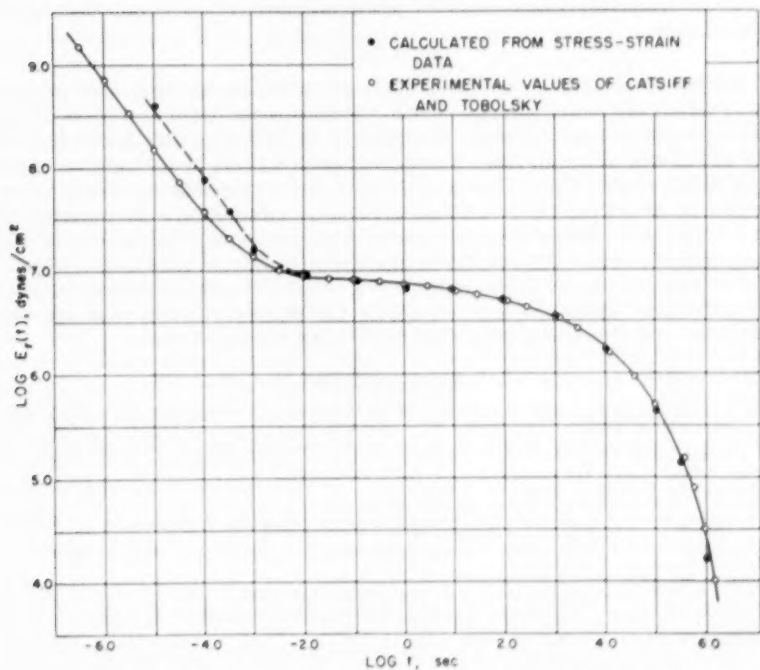


FIG. 9.—Stress-relaxation modulus derived from stress-strain data compared with experimental data of Catsiff and Tobolsky.

two curves should be identical if an unambiguous strain rate in steady flow is employed.) Similar behavior is seen in Figure 8, which shows a plot of $\log S_r$ vs. $\log R$ (the reduced strain has been replaced by $1/R$, which is equivalent to setting γ equal to unity) and a plot of $\log \eta'$ vs. $\log \omega$. (Values of η' were obtained from data reported by Marvin⁵.) It is seen that η' decreases more rapidly than S_R . If, however, the derivative $d(\alpha S)/dR$ is used, this quantity varies with R in almost the same manner as η' varies with ω , as shown in Figure 8. The quantity $d(\alpha S)/dR$ was derived from the reduced stress-strain curve after γ in the reduced strain was equated to unity.

The stress-relaxation modulus $E_r(t)$ was calculated from the reduced stress-strain curve shown in Figure 7 by using Equation (4). The calculated values are shown in Figure 9 along with the experimental values reported by Catsiff and Tobolsky². It is seen that the agreement is excellent in the range $-3.0 < \log t < 6.0$. The calculated values of $E_r(t)$ for $\log t < -3.0$ are inaccurate due to the uncertainty in the reduced stress-strain curve in this range of reduced time.

In order to derive the distribution function $M(\tau)$ from the stress-strain data using the usual approximation methods, it is necessary first to calculate $E_r(t)$, and then $M(\tau)$ can be obtained from $E_r(t)$. Since the distribution function has been calculated previously from the stress-relaxation data shown in Figure 9, as well as from dynamic data^{1,5,16}, the calculation was not repeated.

In conclusion, it has been shown that stress-strain curves, for elongation up to 100 per cent, measured at different strain rates and temperatures, can be superposed to give reliable values of α_T and that the resulting reduced stress-strain curve represents accurately the viscoelastic behavior over nine decades of reduced time.

SYNOPSIS

The use of stress-strain curves to characterize the linear viscoelastic properties of rubberlike materials is discussed. Tensile stress-strain curves for a high molecular polyisobutylene were measured at ten temperatures between -54 and 85°C and at strain rates between 0.104 and $0.104 \times 10^{-3} \text{ sec}^{-1}$. At a single temperature, the data superpose on a double logarithmic plot of stress divided by strain rate against strain divided by strain rate. By superposing data obtained at different temperatures, the temperature dependence of viscosity was obtained. All data for elongation up to 100 per cent were combined to give a single reduced stress-strain curve, which extends over ten decades of reduced time. From the reduced curve, the stress-relaxation modulus was calculated and found to agree satisfactorily with published data.

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ADIABATIC STRETCHING AS A METHOD OF INVESTIGATION OF THE ELASTIC PROPERTIES OF RUBBERLIKE MATERIALS *

M. P. VOTINOV AND E. V. KUVSHINSKIĬ

Evidence of the kinetic nature of rubber elasticity is for the most part derived from data on the relation between the temperature and the forces developed in rubber compounds held under constant elongation throughout a test¹. Thus our concept of the nature of rubber elasticity is based, as a rule, on data which throw only an indirect light on the principles governing the transformation of work into heat and heat into work—data which are of value only when the experimental conditions are reproducible and may be considered to represent thermodynamic equilibrium.

In addition to this, no study has been made of the direct thermodynamic effects which would enable one to determine the nature of elasticity of vulcanizates deformed at finite rates, i.e., under conditions where no thermodynamic equilibrium exists. The reason for this apparently lies in the many experimental difficulties, and, in addition, in the failure to realize the possibility of an analysis ultimately based on thermodynamics and on purely molecular considerations.

The heat effects resulting from stretching rubber were first studied by Joule² about a century ago. However, until recently such investigations were independent of any study of elastic characteristics. Only James and Guth³ have used the data of Dart on the Joule-Gough effect to confirm the qualitative rather than the quantitative kinetic origin of the elasticity of rubber. A similar conclusion regarding the nature of rubber elasticity was reached earlier by Wiegand and Snyder⁴ from an analysis of work with their rubber pendulum—a unique heat machine in which rubber serves as the working part.

In conditions of dynamic stress it is essential to study the principles which underlie the reverse transformation of the heat liberated during elongation back into work. If the internal energy of rubber is governed primarily by the temperature of the vulcanizate and depends little on its deformation, then regardless of how reversible the elongation process may be, the work of deformation (elongation or compression) under isothermal conditions will apparently equal the heat Δq (liberated or absorbed). Under adiabatic conditions the work of deformation is related directly to the corresponding change in temperature Δt , according to the equation:

$$A = \int_{t_1}^{t_2} c \cdot dt \simeq r \cdot c \cdot v \cdot \rho \cdot \Delta t = r \cdot C \cdot \Delta t$$

where A is the work of deformation; C and c are the mean values of the total heat capacity and the specific heat of the stock, respectively; v is the volume;

* Translated from RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from the *Zhurnal Tekhnicheskoi Fiziki*, Vol. 25, No. 12, pages 2157-2162 (1955). The original Russian paper does not give the address of the authors.

ρ is the density; and r is the mechanical equivalent of heat. Evidently this relation holds true in both the elongation and the compression stroke. In some rubber compounds the macromolecules may become oriented with such regularity that the material partially "crystallizes" under strain. In this case the heat effect will be determined by the sum of the work performed on the body, i.e., the work of external forces as well as the work of internal forces of intermolecular reaction. The heat liberated will be greater than the work done on the rubber. This fact is plainly seen in the form of the equation: $rC\Delta t = \Delta q = f_s(A)$.

The greater the difference between the internal work A and the heat Δq , the more a given type of rubber compound differs in its elastic behavior from the "ideal"; i.e., the more it "crystallizes" when stretched.

In compression all the processes should develop in the opposite direction. The existence of irreversible processes is revealed when the work done by compression is less than that by elongation. The cooling during compression will then be correspondingly less than the heating during elongation. Here the final point in the relation: $\Delta q = f_s(A)$ does not agree with the initial one. Its corresponding abscissa and ordinate positions characterize the work transformed into heat in the course of the whole deformation cycle.

The method of isothermal strain is entirely faultless from the theoretical point of view, but experimentally great difficulties are encountered because of the low heat conductivity of rubber compounds. For this reason, the method of adiabatic strain is preferable. In this case the material being tested itself serves as the "calorimeter" in which the heat is given off during elongation (or absorbed during compression).

We set up an experimental apparatus by means of which the temperature of the rubber samples could be measured at the same time that a curve of their elongation was being recorded. The first measurements showed that the losses of heat in the surrounding regions were considerable. We were compelled to make a number of measurements to insure that the strain was adiabatic.

In order to guard against losses of heat occasioned by air convection, which would be important in the experiments, the samples were elongated in a test chamber the interior of which was kept at a pressure of about 10^{-2} to 10^{-3} mm. of mercury.

The moving coupling rod of the machine was connected with the sample clamp by means of a steel bar, which projected into the chamber through an oil seal. The movement of the rod through the oil seal was achieved without any appreciable loss of vacuum inside the chamber. The amount of friction in the seal did not exceed 100 grams. The pressure inside the chamber was measured with the aid of an electrical discharge.

For the testing, large rubber samples were used having a cross-section of 100 sq. mm., made by assembling two double slabs, the length of each unit section being 60 mm.

The temperature was measured with a differential thermocouple connected with a reflecting galvanometer, whose period of free oscillation was 5 seconds. The working junction of the thermocouple was embedded between plies of the rubber, in the center of one section of the sample, in such a way that the thermocouple wire was in contact with the rubber for a considerable length. Thereby the heat resistance of the thermocouple wires was considerably greater than that of the contact between the junction and the rubber. A constantan-manganin thermocouple, made from wires with a diameter of 50μ , was used (the heat conductivity of manganin is 1/15 of that of copper, and is equal to

that of constantan). These precautions reduced the flow of heat along the wires and minimized local cooling of the material next to the junction.

An insulating cover was placed around the test chamber, through which the liquid from the constant temperature bath could flow; this made it possible to conduct measurements at different temperatures. The temperature inside the chamber remained constant during the tests.

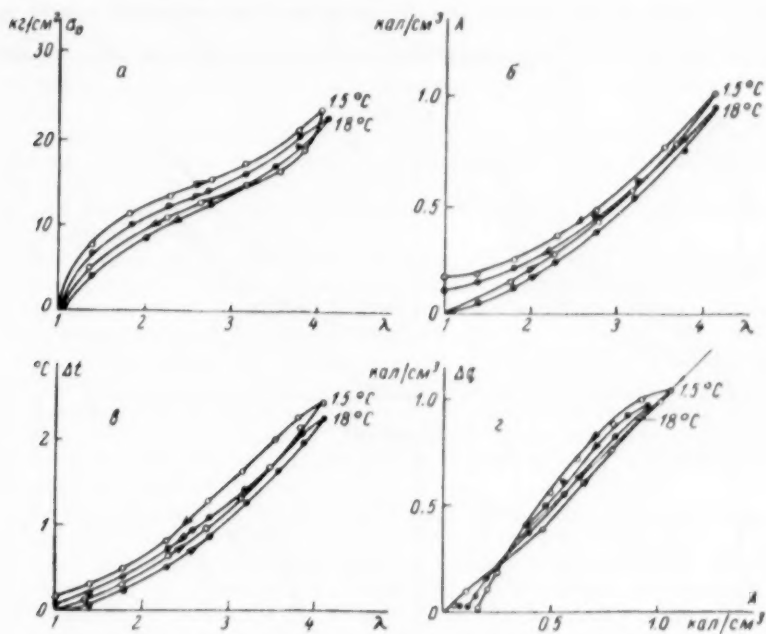


Fig. 1.—An unloaded butadiene-acrylonitrile rubber compound.

Upper left.—Stress-strain curves; the abscissa represents the relative elongation λ , the ordinate the stress σ_0 in kg. per sq. cm.

Upper right.—Relation between work of deformation and degree of elongation; the abscissa represents the relative elongation λ , the ordinate the work of deformation A in cal./cc.

Lower left.—Rise of temperature related to the degree of elongation; the abscissa represents the relative elongation λ , the ordinate the temperature differential Δt in $^{\circ}\text{C}$.

Lower right.—Relation between the quantity of heat liberated and the amount of work done; the abscissa represents the work done in cal./cc., the ordinate the change in the heat liberated Δq in cal./cc.

The measuring procedure was as follows. During the elongation the motion of the clamps, the stress, and the temperature of the sample were simultaneously recorded. The deflection of the clamps in the special experiments was regulated so as to equal the length of one of the unit sections of the sample. (The inertia scheme for measuring the temperature of a sample prevented the mean rate of deformation from exceeding 7 per cent per second.)

The work done in stretching was determined by graphic integration of the stress-strain curves. This work was compared with the amount of heat $\Delta q = rC\Delta t$ generated in the sample. Data on the specific heat and density of rubber were taken from the literature. The total error in the determination of work done and in the calculation of the heat effect did not exceed 10 per cent.

The stocks used for the purpose of checking the method were of two types which have been rather thoroughly investigated: those that are "crystallizing" and "noncrystallizing" under strain. The recipes of these rubber compounds differed from those of industrial compounds in containing no fillers⁶.

The results of this research are presented in the form of the equations:

$$\sigma_0 = f_1(\lambda); \quad A = f_2(\lambda); \quad \Delta t = f_3(\lambda); \quad \Delta q = f_4(A)$$

where σ_0 is the stress, based on the original cross-section area of the sample, in kg. per sq. cm.; $\lambda = \frac{l}{l_0}$ is the elongation per unit section of the sample; A is the

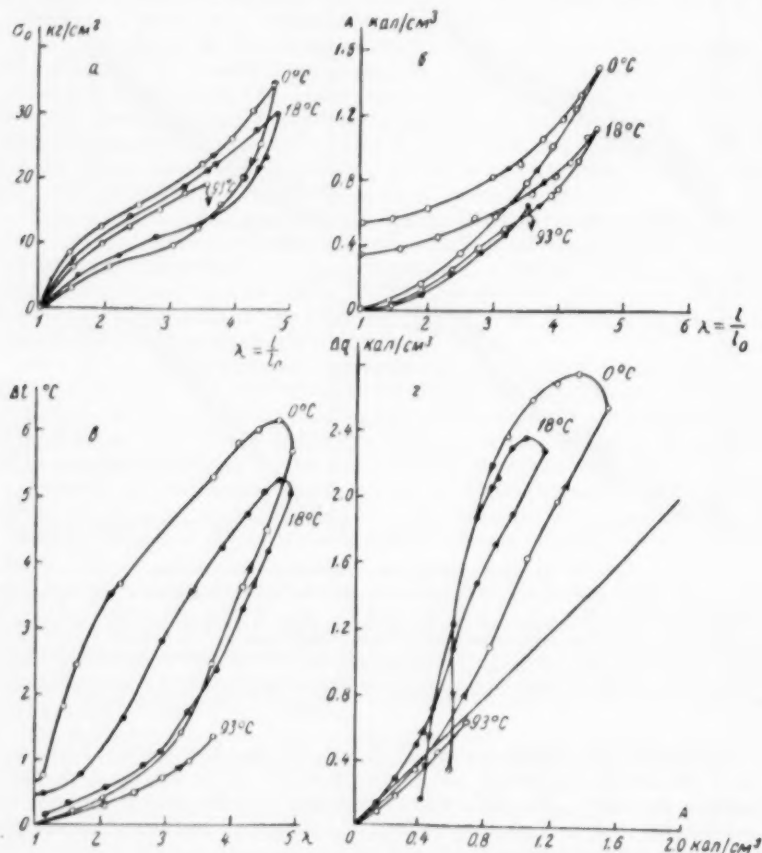


FIG. 2.—An unloaded polychloroprene rubber.

Upper left.—Stress-strain curves; the abscissa represents the elongation λ , the ordinate the stress σ_0 in kg. per sq. cm.

Upper right.—Relation between work of deformation and degree of elongation; the abscissa represents the relative elongation λ , the ordinate the work of deformation A in cal./cc.

Lower left.—Rise of temperature related to the degree of elongation; the abscissa represents the relative elongation λ , the ordinate the change in temperature Δt in °C.

Lower right.—Relation between the quantity of heat liberated and work done; the abscissa represents the work A in cal./cc., the ordinate the heat Δq in cal./cc. The straight line is drawn at a 45° angle from the origin.

work done in elongation in calories per cu. cm.; Δt is the change of temperature of the sample in $^{\circ}\text{C}$; and Δq is the heat generated, in calories per cc.

In Figure 1, parts *a*, *b*, *c*, and *d* show the basic relationships found at different temperatures for unloaded butadiene-acrylonitrile rubber compounds.

It is evident that the stress-strain curves have a "creeping" character. The modulus of elasticity is not very high, and changes only a little with changes of temperature. Only a slight hysteresis effect is evident in elongation and compression. The maximum limit for the elongation is the onset of break. Because of lack of stiffness of the compound, the work done in elongation is small. For example, the maximum value for the work done at 18°C is about 1.06 calories per cc., and the rise of temperature resulting from this equals about 2.3°C .

In elongation, the heat generated corresponds almost exactly to the mechanical work done on the sample; in compression, likewise, the heat loss observed corresponds to the amount of work done by the sample. This was found to hold true for both loaded and unloaded compounds of either polybutadiene or butadiene-styrene rubber.

By putting these facts together one may conclude that the elasticity is kinetic in origin. In their elastic behavior such compounds should conform to the kinetic theory of elasticity. They differ from "completely" elastic rubbers only in the presence of a hysteresis effect.

We likewise studied unloaded compounds of natural rubber (smoked sheet and kok-saghyz) and two polychloroprene compounds at various temperatures.

The stress-strain curves are S-shaped. The work is a function which increases rapidly with elongation. The hysteresis is appreciable here. The rise of temperature is markedly greater than in the first case, and depends on the temperature of the experiment.

In Figure 2, parts *a*, *b*, *c* and *d* show examples of the basic relations that hold true of unloaded polychloroprene compounds at three temperatures.

The relation $\Delta q = f_4(A)$ has a different character in "crystallizing" than in "noncrystallizing" materials. In "crystallizing" compounds we observe not only a reversible generation (or absorption) of heat according to the external work done, commencing at a certain degree of elongation, but also a generation of excess heat, which increases with the elongation.

The latter fact indicates a change in the reaction energy of polymer molecules, which is connected with partial crystallization of the material. In compression we note a retardation in the breakdown of the "crystalline" phase formed. By measuring the temperature during the experiment, one may shift the onset of the crystallizing processes into regions of large elongations and large quantities of mechanical work.

In all cases the points for the equation: $\Delta q = f_4(A)$, corresponding to the termination of the experiment, are located slightly below a straight line drawn at a 45° angle from the origin. The introduction of corrections for cooling and for the inertia of the measuring apparatus have little effect on the character of this equation, although it does displace the points onto the straight line. Hence we have omitted such corrections in the present work.

The experimental data presented attest that the assumptions made as a basis for the method are justified, and that the method of adiabatic strain may prove to be a useful tool for the study of the elastic characteristics of rubberlike materials.

CONCLUSIONS

1. A direct method has been proposed for the study of the elastic characteristics of rubber stocks under nonequilibrium deformation conditions.

2. This method has been successfully applied in the study of the elastic characteristics of "crystallizing" and "noncrystallizing" unloaded rubber compounds.

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- ³ James and Guth, *J. Chem. Physics* **2**, 455 (1943); *RUBBER CHEM. & TECHNOL.* **16**, 266 (1943).
- ⁴ Wiegand and Snyder, *Trans. Inst. Rubber Ind.* **10**, 234 (1934); *RUBBER CHEM. & TECHNOL.* **8**, 151 (1935).
- ⁵ How large these losses are can be seen, for example, from an analysis of Joule's data (*Phil. Trans.* **149**, 91 (1859)), which were obtained by testing fairly thin ring-shaped samples of vulcanized rubber. The work of deformation, at 567 per cent elongation, was five times as great as the heat effect, which was measured directly.
- ⁶ The samples for these experiments were furnished by the S. V. Lebedev All-Union Scientific Research Institute for Synthetic Rubber.

DYNAMIC-MECHANICAL CHARACTERISTICS OF RUBBER COMPOUNDS *

S. DE MEY AND G. J. VAN AMERONGEN

RUBBER-STICHTING, DELFT, NETHERLANDS

INTRODUCTION

Many rubber products, such as truck tires, vibration dampers, and conveyor belts, are used under conditions where the rubber is subjected to small periodic deformations. For this reason great interest attaches to the mechanical properties of various rubber compounds and plastics measured under alternating loads.

This subject has not only a practical side but also a theoretical one. A theory has been developed according to which the mechanical behavior under alternating loads can be represented as a combination of elastic and viscous deformation.

The models of Maxwell and Voigt are the most familiar ones for the description of this theory¹. With this theory the static modulus and the dynamic modulus of elasticity can be related to a distribution function of relaxation or retardation times². Such a relaxation spectrum is very difficult to determine exactly by measurement, but various approximate methods of calculation have been described³.

The knowledge of the relaxation spectrum is of theoretical interest chiefly because it makes it possible in principle to calculate and correlate all the time-dependent characteristics, such as creep, relaxation, and elastic after effect⁴. The approximate values obtained are too inaccurate, however, and the mathematical calculations themselves too complicated to be of practical importance.

The number of methods employed to measure the dynamic-mechanical characteristics is very large. These investigations have been carried out in many directions. Many measurements on the temperature and frequency dependence are known. Gehman⁵ investigated the importance of the dynamic characteristics of rubber for vibration dampers. Roelig and Heidemann⁶ have pointed out the possibility of the evaluation of these properties in copolymers for analytical purposes, while Ecker⁷ made measurements to determine the reinforcing action of numerous fillers and the effect of initial static stress on the dynamic characteristics of different types of rubber.

Schmieder and Wolf⁸ studied the behavior of a large series of high polymers and the influence of crosslinking on the properties of natural rubber. Fitzgerald and Ferry⁹ investigated the influence of softeners in synthetics. The effect of softeners on the second-order transition point of natural rubber was tested by Fletcher, Gent, and Wood¹⁰.

The present paper gives a systematic discussion of the test results of the dynamic modulus of elasticity of rubber compounds of different composition,

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as a function of static initial load, shape of the rubber samples, frequency, temperature, and amplitude.

SOME PHYSICAL PRINCIPLES

If the oscillating force acting on the rubber is a sinusoidal function of the time with frequency f , then in general the deformation will also be sinusoidal and of the same frequency. However, there will be a phase displacement δ (Figure 1). The equation for stress σ and relative deformation ϵ are as follows:

$$\sigma = \sigma_0 \exp j\omega t \quad (1a)$$

$$\epsilon = \epsilon_0 \exp j(\omega t - \delta) \quad (1b)$$

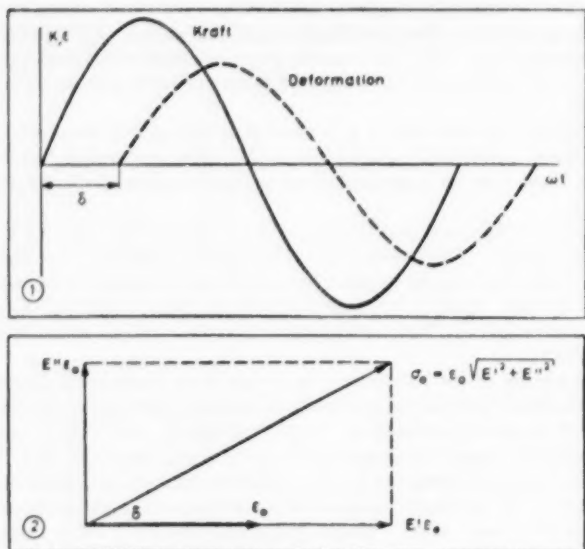


FIG. 1.—Alternating force K and deformation ϵ as functions of time.

FIG. 2.—Vector diagram showing the relation between stress σ , deformation ϵ , and modulus of elasticity E .

where $\omega = 2\pi f$ = angular velocity, σ_0 = force amplitude, ϵ_0 = deformation amplitude, and t = time.

The complex modulus of elasticity E can be calculated by the equation:

$$\frac{\sigma}{\epsilon} = E = E' + jE'' \quad (2)$$

(Figure 2) in which the dynamic E' modulus represents the component of E in phase with the deformation. The E'' modulus is the component of E which is displaced 90° with respect to the in-phase deformation. E'' can be regarded as a measure of the hysteresis losses, or damping resulting from the internal friction of the rubber molecules. From Equation (3):

$$E'' = \omega \cdot \eta \quad (3)$$

E'' can be related to the intrinsic viscosity η of the rubber.

Another measure of the damping which we shall also make use of in what follows is the loss factor:

$$\tan \delta = E''/E' \quad (4)$$

These ideas and equations are analogous to those in customary use in electrical theory and in explaining the dielectric behavior of materials.

The use of the complex dynamic modulus as a material constant has the advantage that the behavior of rubber can be calculated in advance, provided the modulus is known as a function of the different variables, such as temperature, frequency, and amplitude, and the conditions are specified. Thus, for example, the heat build-up in rubber under alternating load, as investigated, among others, by Springer¹¹ and by Kainradl and Haendler¹², can be expressed in terms of these quantities. It is given by the integral of the work performed per cycle:

$$\int \sigma_0 \sin \omega \cdot t \cdot d \{ \epsilon_0 \sin (\omega \cdot t - \delta) \} \quad (5)$$

and amounts to:

$$W = \pi \cdot E'' \cdot \epsilon_0^2 \cdot f \quad (6)$$

per second per unit volume.

METHOD OF MEASUREMENT

An outline of the methods for measuring the dynamic properties of rubber-like materials has been given, among others, by Marvin¹³. Many of the types of apparatus have the evident drawback that the test conditions and also the nature of the deformation are not sufficiently well defined so that the results can be considered only rather roughly approximate values.

The oscillatory test apparatus used in our experiments, with which the above mentioned test conditions can be determined unambiguously, was devised in our Institute by J. A. J. Bronkhorst. It combines the principles of the Stambaugh apparatus¹⁴, in which the rubber is tested under compression, and the apparatus of Dillon, Prettyman, and Hall¹⁵, with which the rubber can be tested while under shear loading.

Figure 3 gives a schematic representation of the apparatus, of which a photograph is shown in Figure 4. The two rubber samples K are clamped between two solid plates A and a cross-shaped body B. A magnetic vibrator produces forced sinusoidal vibrations in B and in a rod on which weights G of different sizes can be fastened. The whole system is suspended on steel wires. In this case the rubber is tested under compressive load and used as the spring of a vibrating mass-spring system. The inertia of the rubber can be neglected, since the wave length of the vibrations within the frequency range of the apparatus is large compared to the dimensions of the rubber sample.

The use of two rubber samples (K, K) has the advantage that the effect of any possible nonlinear course of the stress-strain curve is cancelled in such a way that the second harmonic vibration cannot appear. ["Push-pull", Translator]

The force required by the vibrator for the oscillation is furnished by the current in the driving coil. This current, passing through the resistance R, produces a voltage which is applied to an oscillograph and which acts on the vertical coordinate of the picture screen. The horizontal axis shows the alter-

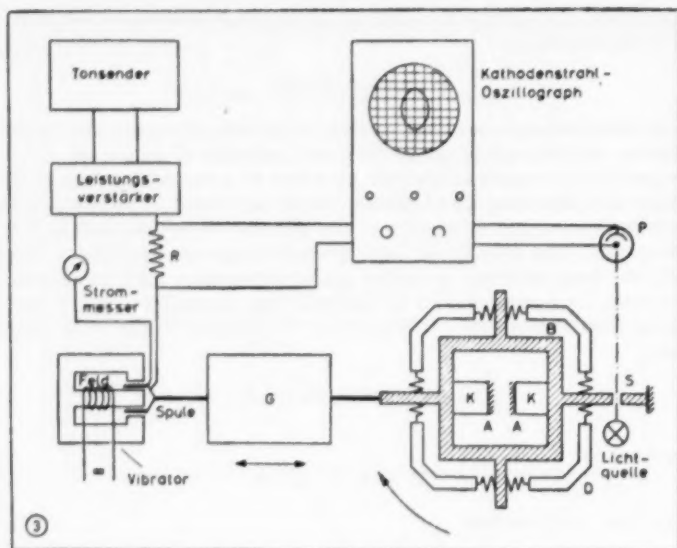


FIG. 3.—Schematic representation of the vibration apparatus with accessories.

nating voltage from a photocell P. This alternating voltage, which is excited by a beam of light interrupted by the varying slit S, is a measure of the amplitude of the rubber sample. The result on the oscilloscope screen is an ellipse. The measurement is taken at resonance, that is, with the ellipse vertical. This adjustment is made by varying the frequency for a given constant weight G. The amplitude is determined either by a microscope or with an electronic strain gage¹⁶.

The clamping arrangement A-B is contained in an air thermostat D. The openings for the connections with the vibrator are sealed with unstressed mem-

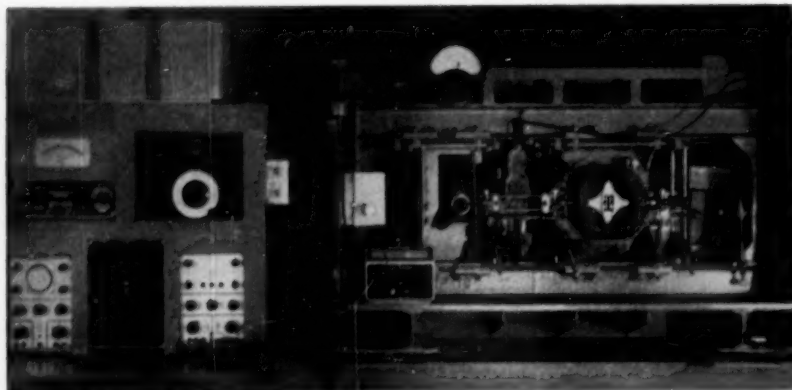


FIG. 4.—Photograph of the vibration apparatus with accessories.

branes. Besides compressive loading, the rubber can also be tested under shear loading. This is done by turning the chamber D 90° in the direction of the arrow, without making any changes in the rubber itself. The static initial load can be set at any desired value by means of the support plates A.

The whole apparatus is mounted vibration-free on rubber.

Frequency range about 5 to 200 cycles per sec.

Temperature range -40° to 100° C.

Maximum amplitude of alternating force 10⁷ dynes.

Maximum height (h_0) of the rubber samples 10 mm., maximum diameter (D_0) 20 mm.

The shape factor is defined as $D_0/4h_0$ and in all cases lies between 0.1 and 1.25.

The components E' and E'' of the complex modulus E are determined by means of the described apparatus as follows:

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{S}{m}} \quad (7)$$

$$S = E'(F_0/h_0) \quad (8)$$

$$E'' = (K/a)(h_0/F_0) \quad (9)$$

f_0 = resonance frequency (cycles per sec.)

S = stiffness of rubber (dynes per cm.)

m = mass of weight G (g.)

F_0 = compression surface of rubber sample (cm.²)

h_0 = height of rubber sample (cm.)

K = force exerted by the vibrator on the rubber at resonance (dynes)

a = amplitude of vibration (cm.)

COMPOSITION OF THE COMPOUNDS

Tables I and II give the composition of the rubber compounds studied. The Butyl-rubber compound B₂ was mixed and vulcanized in the normal manner and then once more according to the Gessler hot process¹⁷. In this method the

TABLE I
COMPOSITION OF THE NATURAL-RUBBER COMPOUNDS
(PARTS BY WEIGHT)

Compound	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉	A ₁₀	A ₁₁
Natural rubber (smoked sheet)	100	100	100	100	100	100	100	100	100	100	100
Vulcan-3 (HAF)	—	20	50	—	—	—	50	—	—	—	—
Vulcan-9 (SAF)	—	—	—	50	—	—	—	—	—	—	—
Spheron-9 (EPC)	—	—	—	—	50	—	—	—	—	—	—
Styrene-butadiene (85/15) copolymer	—	—	—	—	—	—	—	—	—	—	50
Aniline resin	—	—	—	—	—	—	—	25	43	—	—
Aerosil	—	—	—	—	—	—	—	—	—	40	—
Sulfur	2	2	2	2.5	2.5	—	—	2	2	3	2.5
Tetramethylthiuram disulfide	—	—	—	—	—	4	4	—	—	—	—
Stearic acid	2	2	2	2	2	2	2	1	1	—	2
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5
Phenyl-2-naphthylamine	1	1	1	1	1	1	1	1	1	1	1
Santocure	1	1	1	0.9	0.9	—	—	1	1	3	1
Dutrex-55	—	2	2	3	2	—	3	2	2	—	—
Akticel-A	—	—	—	—	—	—	—	—	—	4	—
Vulcanization temp. (°C)	142°	142°	142°	142°	127°	142°	142°	142°	142°	142°	142°
Vulcanization time (min.)	20	20	20	30	45	25	25	20	20	30	30

mixing of the carbon black into the rubber is interrupted 6 hours, during which the batch is heated at 160° C in a steam autoclave. It is claimed that the mechanical properties of Butyl-rubber vulcanizates containing EPC carbon black are markedly improved by this treatment.

We have also included in these studies Vulkollan having 72 Shore A hardness.

INFLUENCE OF STATIC COMPRESSION AND SHAPE OF TEST-SPECIMEN

It was established that the values found for the E' modulus are dependent not only on the composition of the rubber compounds, but also, to a considerable degree, on the static compression and on the shape of the rubber samples.

TABLE II
COMPOSITION OF THE SYNTHETIC-RUBBER COMPOUNDS
(PARTS BY WEIGHT)

Compound	B ₁	B ₂	C ₁	C ₂
Butyl rubber	100	100	—	—
GR-S cold rubber (Polysar Krylene)	—	—	100	100
Vulcan-3 (HAF)	—	—	—	50
Spheron-9 (EPC)	—	50	50	—
Sulfur	2	2	2	2
Tetramethylthiuram disulfide	1	1	—	—
Stearic acid	1	0.5	—	2
Zinc oxide	3	5	3	5
Phenyl-2-naphthylamine	—	—	1.2	1
Santocure	—	—	1.65	1.6
Dutrex-55	—	—	—	5
Mercaptobenzothiazole	0.5	—	—	—
Asphalt	—	—	4	—
Benzothiazolyl disulfide	—	1	—	—
Vulcanization temp. (° C)	152	153	142	142
Vulcanization time (min.)	45	60	45	40

Figure 5 shows the E' modulus as a function of the relative static compression ϵ_1 , for different shape factors $D_0/4h_0$, as found at room temperature from compression measurements on an unfilled vulcanized natural-rubber compound (compound A₁). The E' modulus here has been calculated from the stiffness and the original dimensions of the rubber samples. This apparent value $E'_{(\epsilon_1)}$ depends, theoretically, therefore, in the case of incompressible rubber on ϵ_1 according to Equation (10):

$$E'_{(\epsilon_1)} = \frac{E'_{(0)}}{(1 - \epsilon_1)^2} \quad (10)$$

where it is assumed that the value $E'_{(0)}$, calculated for the actual dimensions, represents a material constant. The family of curves in Figure 5 shows a satisfactory agreement with this, while the deviations at higher values of ϵ_1 and $D_0/4h_0$ can be attributed to the fact that the cylindrical samples are more or less deformed into a barrel-shaped figure by the disturbance of the lateral movement of the circular faces.

The influence of the shape factor on the actual E' modulus can be seen from Figure 5. By plotting the values of E' obtained by extrapolating to zero static stress as a function of the shape factor, we get Figure 6. This figure also shows values for the dynamic shear modulus (G' modulus) for the same rubber

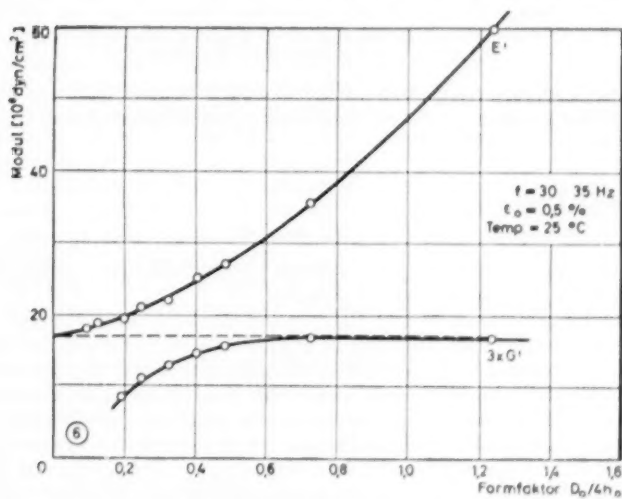
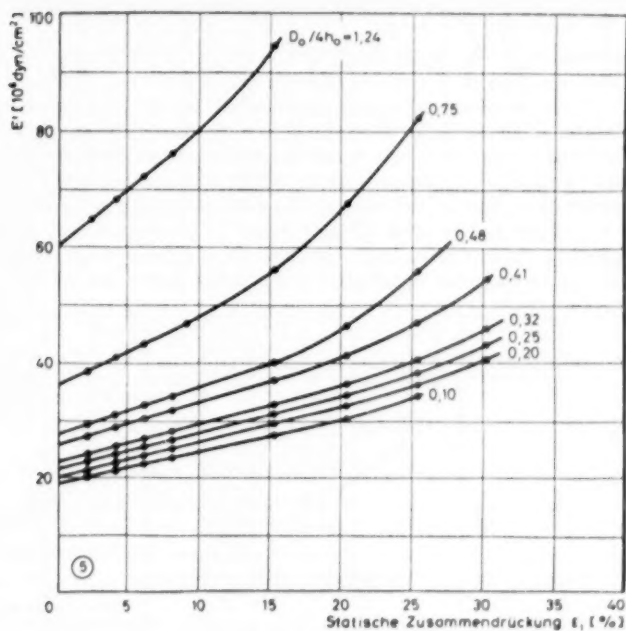


FIG. 5.—Modulus of elasticity E' of an unfilled natural-rubber compound as a function of the static compression of the rubber samples for different shape factors.

FIG. 6.—Elasticity and shear moduli of an unfilled natural-rubber compound as functions of the shape factor at 0% static compression.

samples. These values were obtained in a similar manner by shearing experiments.

The increase in E' for short samples is a result of the change to a barrel shape already mentioned, by which the effective height is less than the true height h_0 ¹⁹. Long slender samples are only slightly affected by this, so that the true E' modulus at shape factor zero and $\epsilon_1 = 0$ results. The shape is without effect on the loss factor, since this is the dimensionless quotient of two moduli which depend on shape to the same extent. The measurements confirmed this.

The deviation of the G' modulus in the case of slender samples with low values of the shape factor must be attributed to the occurrence of flaws in combination with the shearing load. In this case a correct value for use in the calculations can be obtained at a higher shape factor figure (e.g., 0.8).

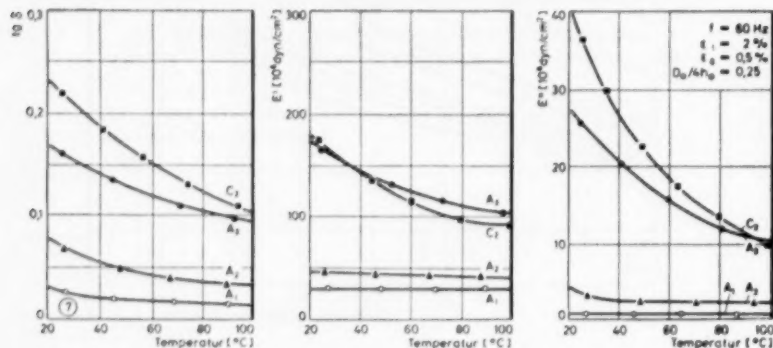


Fig. 7.—Loss factor and modulus of elasticity of various rubber-HAF carbon black compounds as functions of the temperature.

When we compare the values for the E' and G' moduli obtained by extrapolation in this manner it is found that a very good approximation is given by Equation (11).

$$E' = 3G' \quad (11)$$

The theoretical value is:

$$E' = 2(1 + \mu) \cdot G' \quad (12)$$

From Equations (11) and (12) the Poisson ratio comes out $\mu = 0.5$, the theoretical value for an incompressible material.

If these measurements clearly indicate the incompressibility of an unfilled natural-rubber vulcanizate, they are, on the other hand, also a proof of the reliability of our apparatus. They show in addition that in the explanation of the results of dynamic measurements one must observe the necessary caution, when the absolute values of the modulus are in question. Static initial stress, sample shape, and amplitude of oscillation, whose importance will be discussed in more detail, play an important role in this regard. For this reason it is necessary to carry out dynamic measurements under clearly specified conditions. Comparative measurements with different rubber compounds should be made only under identical conditions.

In the following measurements the experimental conditions are always stated. The results have not, however, been corrected for shape factor and static initial stress.

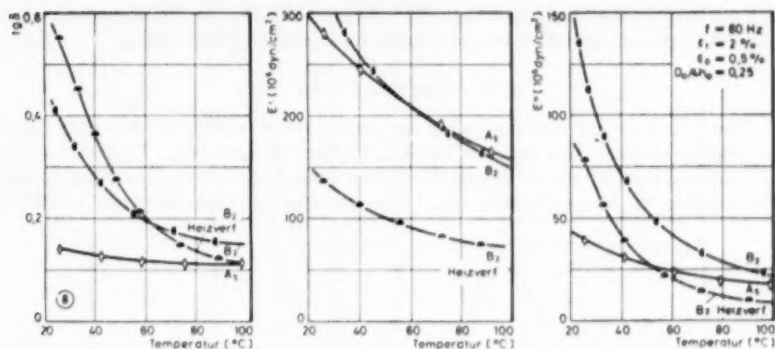


FIG. 8.—Loss factor and modulus of elasticity of a natural rubber-EPC carbon black compound compared with those of Butyl rubber as functions of the temperature.

INFLUENCE OF TEMPERATURE

RANGE OF 20° TO 100° C

The influence of temperature in the range 20° to 100° C on the loss factor $\tan \delta$ and on the two components of the E modulus of natural rubber and GR-S (cold rubber) reinforced with HAF carbon black, as well as the influence of the HAF carbon black content are shown in Figure 7 (compounds A_1 , A_2 , A_3 , and C_2).

The stiffening action appears only at higher carbon black contents, and in this region there is a marked rise of the loss factor. The loss factor of GR-S (cold rubber) is larger than that of natural rubber.

Figure 8 shows the dynamic characteristics of Butyl rubber reinforced with 50 parts EPC carbon black which had been mixed according to the Gessler hot process¹⁷. For comparison, the results are shown for a similar compound not given the heat treatment, and for natural rubber reinforced with the same black (compounds B_2 and A_3).

The loss factors of the Butyl-rubber compounds are considerably greater than those of natural-rubber compounds, but this difference decreases markedly as the temperature is raised. A surprising and even unexpected effect is the much lower E' modulus of Butyl rubber mixed according to the Gessler hot process compared with that shown by Butyl rubber with the normal treatment. It will be shown that this behavior is observed only at very low amplitudes

TABLE III

EXPERIMENTAL CONDITIONS IN THE MEASUREMENTS SHOWN IN FIGURE 9

No.	Compound	Shape factor ($D_2/4h_2$)	Amplitude (%)	Frequency (cycles per sec.)
A_3	Natural rubber-50 EPC	0.12	0.1	50-110
C_1	GR-S cold rubber-50 EPC	0.12	0.5	40-120
B_1	Unfilled Butyl rubber < 20° C	0.25	0.2	30-50
	> 20° C		0.5	40
B_2	Butyl rubber-50 EPC	0.25	0.2	65-145
—	Vulkollan	0.25	0.01	30-130

Static compression ϵ_1 was 2% in all cases.

(0.5 per cent in this case) and that the values of the two moduli approach each other at higher amplitudes or even show the opposite relationship.

RANGE DOWN TO -40°C

The effect of low temperatures on the dynamic characteristics has been thoroughly studied on a series of typical rubber vulcanizates. Difficulties are encountered here which are caused by the extremely pronounced increase in the E' modulus at low temperatures. The resonance point becomes unstable

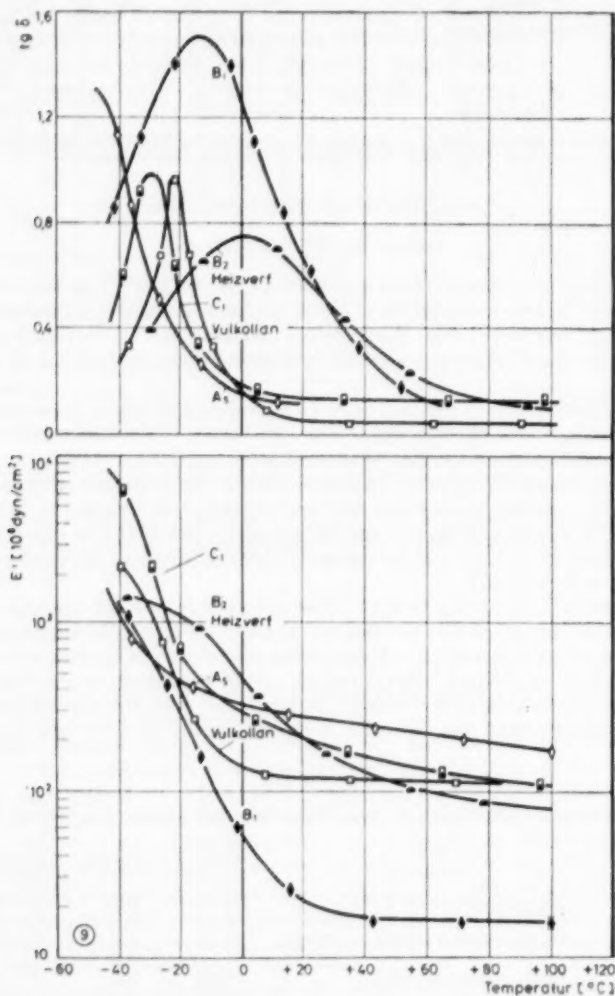


Fig. 9.—Loss factor and modulus of elasticity of various rubber compounds as functions of the temperature in the vicinity of the second-order transition point.

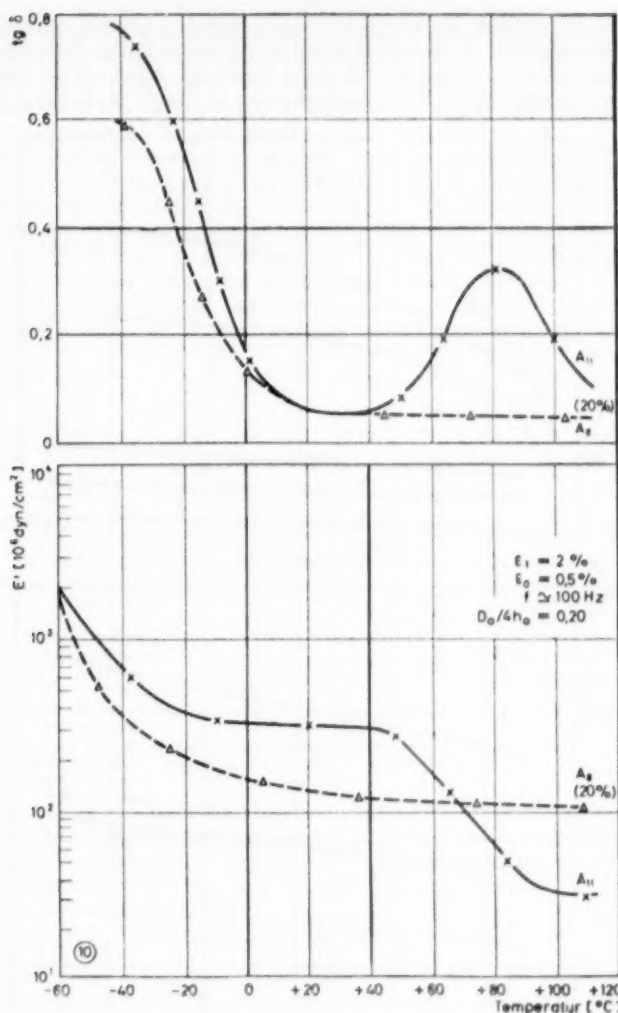


Fig. 10.—Loss factor and modulus of elasticity of a natural rubber-resin (styrene-butadiene 85/15 copolymer) compound compared with those of a natural rubber-aniline resin compound as functions of the temperature.

(labile) because of this pronounced increase. Moreover, because of the limited choice of the weights G , it is not possible to hold the frequency exactly constant within a series of measurements. Both disturbing factors make it impossible to obtain exact values for the dynamic moduli in the neighborhood of the transition point. Nevertheless, since these factors act in the same direction for the different types of rubber and since the conditions for each curve are chosen as nearly identical as possible, we can still make comparisons. Table III shows the rubber compounds selected and the conditions of test. Figure 9, in which the

temperature range from 20° to 100° C is also included, gives a comprehensive picture of the results. It shows the familiar maximum in the curve of the loss factor in the vicinity of the second-order transition point. This maximum, which is, moreover, related to a sharp increase of the E' modulus, invariably

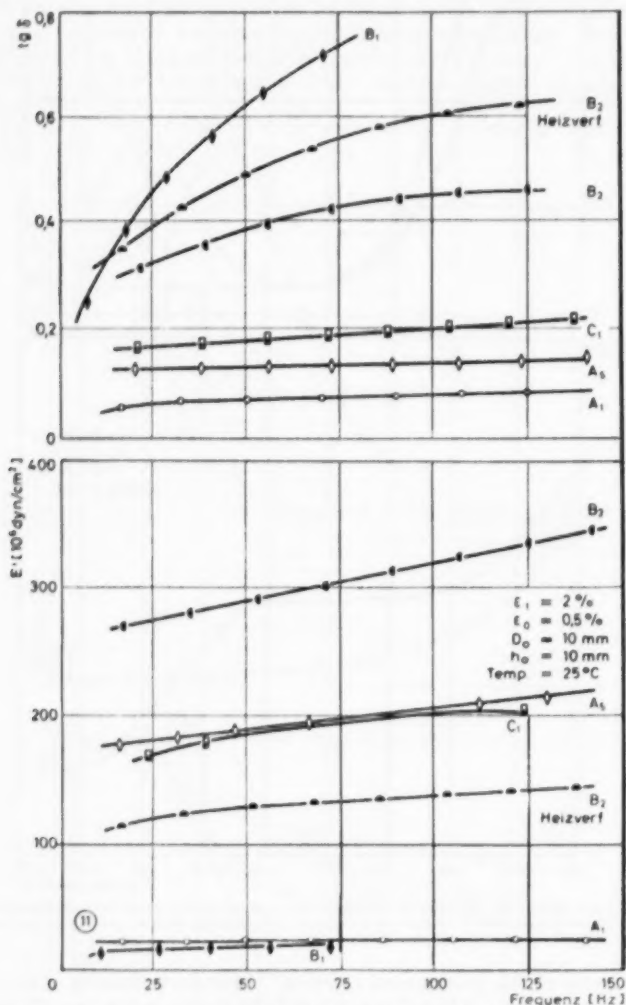


FIG. 11.—Loss factor and modulus of elasticity of several rubber compounds as functions of the frequency.

appears at higher temperatures for the synthetic rubber vulcanizates than for natural rubber.

The influence of the maximum manifests itself also at higher temperatures. The hysteresis losses of natural rubber at room temperature, which are noted

to be low compared with those of most synthetic rubber types, are directly related to the low temperature position of the maximum.

The temperature at which the loss factor maximum occurs depends mainly on the nature of the rubber type. The influence of the different fillers on the position and shape of the peak is only slight.

Figure 10 gives the results of measurements on a natural-rubber compound with aniline resin²⁰ (compound A₈) and on a natural-rubber compound with a resinlike styrene-butadiene (85/15) copolymer (compound A₁₁). Compound A₁₁ shows two maxima in the loss factor, one of which is characteristic of natural rubber, the other of the copolymer. The natural rubber-aniline resin compound does not show any second maximum in the temperature range studied, presumably because the second-order transition point, if this exists at all for aniline resin, can be found only at much higher temperatures.

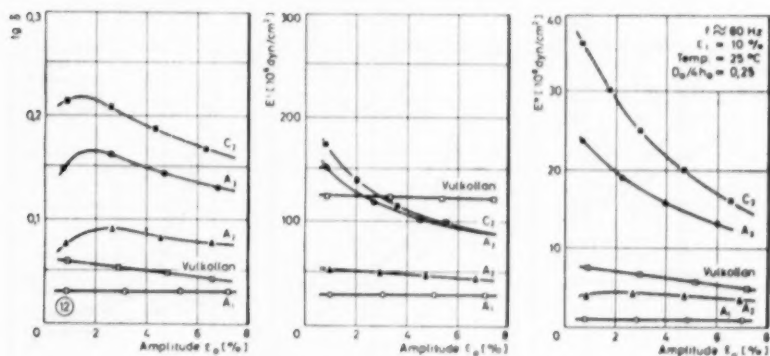


Fig. 12.—Loss factor and modulus of elasticity of various rubber compounds as functions of the amplitude ϵ_0 .

The existence of a second maximum in the region of the transition temperature up to about 150° C makes a compound unsuitable for tires, since because of the positive temperature coefficient no thermal equilibrium can be established, and therefore a destructive heat build-up can take place.

INFLUENCE OF FREQUENCY

The frequency dependence of the loss factor and the modulus of elasticity for compounds A₁, A₈, B₁, B₂, B₃ by the hot process, and C₁ is shown in Figure 11. Only Butyl rubber shows a marked frequency dependence in the measured range. This dependence is a result of the strong influence of temperature (see Figure 9) on the properties of Butyl rubber.

In general, raising the frequency has an effect similar to that of lowering the temperature.

INFLUENCE OF AMPLITUDE

Many investigators have demonstrated the fact that the dynamic characteristics are markedly dependent on the amplitude of the vibrations²¹. Figure 12 shows this dependence on the amplitude of deformation ϵ_0 , as measured on compounds A₁, A₂, A₃, C₂, and Vulkollan. In these measurements the frequency

at the smallest amplitudes was about 70 cycles per second. At higher amplitudes it was somewhat lower. The effect of this difference on the E modulus can be neglected.

The practical importance of the observed amplitude dependence lies in the fact that in all cases where a reinforced rubber compound is exposed to vibration, there is a decrease of stiffness with increasing amplitude which must be taken into consideration. In the production of vibration dampers designed to impart a low resonance frequency to the system to be isolated, this is a favorable factor, since the resonance frequency is shifted to lower values with increasing amplitude.

The behavior of the loss factor is completely dependent on the ratio of the two components of the E modulus. Although the curve can assume different shapes, a maximum at an amplitude of about 1.5 per cent is typical for a reinforced compound.

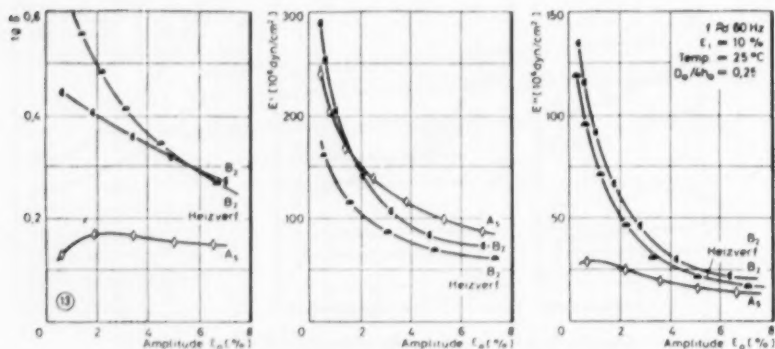


FIG. 13.—Loss factor and modulus of elasticity of a natural rubber-EPC carbon black compound compared with those of Butyl rubber as functions of the amplitude ϵ_a .

Figure 13 shows the results of measurements on Butyl rubber vulcanizates filled with EPC carbon black. Although it is known that the modulus at 300 per cent elongation of the Butyl-rubber compound treated by the Gessler hot process is greater than the modulus of the untreated compound, both the dynamic E' modulus at small amplitudes and the hardness are markedly smaller in the treated compound than they are in the untreated compound. If we compare this with the lower E'' modulus also found by Gessler¹⁷ we find that, although the loss factors do not differ appreciably, they are, nevertheless, greater than in the case of natural rubber.

With increasing amplitude the E' moduli of the treated and untreated Butyl rubber compounds approach each other. From the fact that the additional stiffening of the treated compound shows up only at high amplitudes and elongations one would be inclined to conclude that the number of strong bonds between carbon black and the polymers has been increased by the heat treatment, while the number of weaker bonds has decreased.

Besides the composition of the rubber compound there are a number of other factors which influence the dependence of the dynamic characteristics on the amplitude.

HEAT DEVELOPMENT

Of primary importance is the rise of temperature resulting from the heat development in rubber under vibration loading. Although the heat evolution is often very small and consequently can be neglected, at greater amplitudes it reaches a considerable magnitude, since, according to Equation (6) it increases in proportion to the square of ϵ_0 , the amplitude of deformation.

Provided λ the coefficient of heat conductivity is known, then by using Equation (6) and making a number of simplifying assumptions (among others, the absence of lateral heat conduction and uniform heat production) the tem-

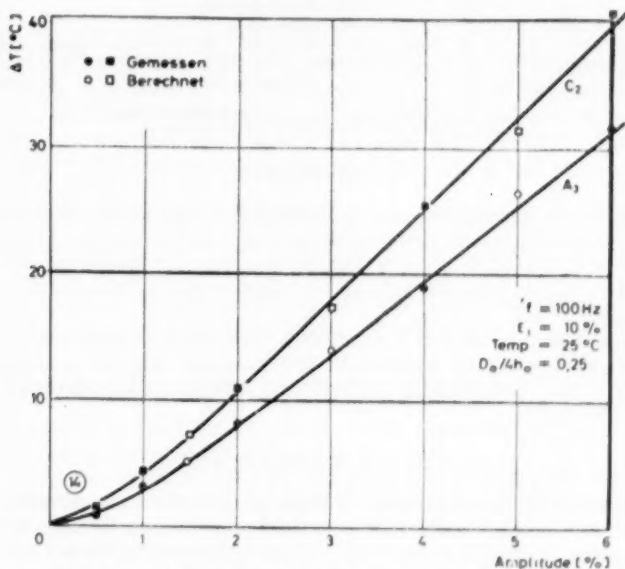


FIG. 14.—Temperature rise in the center of samples of a natural rubber-HAF carbon black compound and a GR-S-HAF compound as functions of the amplitude ϵ_0 .

perature increase ΔT in the center of the vibrating rubber sample can be calculated as follows:

$$\Delta T = A \frac{\pi E'' \epsilon_0^2 f h_0^2}{8 \lambda} \quad (13)$$

where A represents a factor relating to the deviations between the measured and the theoretical values.

Figure 14 shows the temperature rise measured by a thermocouple in the center of the samples as a function of the amplitude for compounds of natural rubber (A_3) and GR-S cold rubber (C_2) with 50 parts of HAF carbon black. The values are those calculated by Equation (13) with $A = 0.385$ and $\lambda = 0.192 \times 10^5$ and 0.207×10^5 erg/cm.-sec.-deg.C, respectively. As shown by Gui, Wilkinson, and Gehman²² and also by the above results, this temperature rise is not sufficient to account for the considerable decrease of the E' and E'' moduli for the reinforced compounds represented in Figure 12 (see also Figure 7).

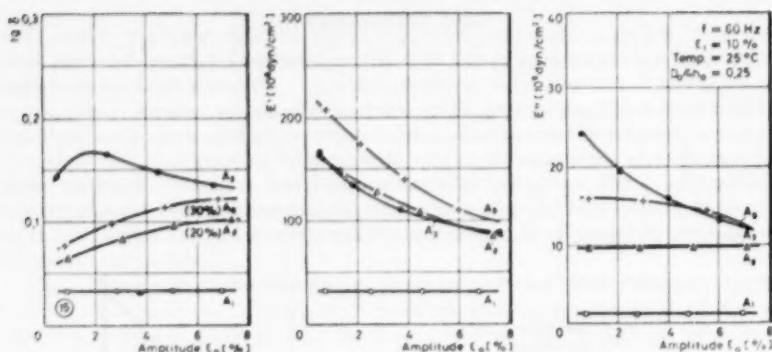


FIG. 15.—Loss factor and modulus of elasticity of natural rubber-aniline resin compounds as functions of the amplitude ϵ_0 .

NONLINEARITY

An amplitude dependence can be attributed to the nonlinear stress-strain curve²³. As already stated, this possibility is excluded by the use of the apparatus described in this work, since, unlike, for example, the Roelig apparatus, this one uses two rubber samples, so that the effect of any existing nonlinearity is largely balanced out.

In support of this claim is the fact that with our apparatus force and amplitude are always exactly sinusoidal. The material behaves, therefore, as if absolutely linear, but exhibits, nevertheless, different characteristics at the different amplitudes.

RUPTURE OF MOLECULAR BONDS

The pronounced decrease of the E modulus of the two components is to be attributed, as is now generally done, to a third phenomenon, namely, to rupture of the bonds in the rubber compound. This rupture can be related both to the rubber-filler bonds and to the filler-filler bonds. From both Figure 12 and

TABLE IV
DYNAMIC CHARACTERISTICS OF SEVERAL NATURAL-RUBBER COMPOUNDS

No.	Compounds	E' in 10^8 dynes/cm. ²				$\tan \delta$			
		25° C		70 c.p.s.		25° C		70 c.p.s.	
		20 e.p.s.	100 e.p.s.	25°	80°	20 e.p.s.	100 e.p.s.	25°	80°
A ₁	NR-unfilled	23	23	23	22	0.03	0.03	0.03	0.03
A ₂	NR-50 HAF	160	175	170	110	0.15	0.16	0.16	0.11
A ₄	NR-50 SAF	265	290	265	160	0.16	0.17	0.17	0.13
A ₅	NR-50 EPC	270	285	280	175	0.13	0.14	0.14	0.12
A ₆	NR-20% aniline resin	118	121	119	102	0.05	0.06	0.06	0.04
A ₉	NR-30% aniline resin	175	183	180	135	0.065	0.07	0.07	0.06
A ₁₀	NR-40 Aerosil	298	302	300	240	0.07	0.08	0.09	0.08
A ₆	NR-unfilled-Thiuram	27	29	28	28	0.07	0.08	0.07	0.05
A ₇	NR-50 HAF-Thiuram	168	182	175	128	0.21	0.21	0.21	0.19

In this table, the abbreviation NR represents natural rubber, and the abbreviation c.p.s. represents cycles per second.

Figure 15, in which the amplitude dependence of natural rubber reinforced with aniline resin is shown (compounds A₈ and A₉) it can be seen that the dependence of the E' modulus of each compound containing reinforcing fillers is the same, whereas the modulus of the unfilled rubber compounds (natural rubber and Vulkollan) is independent of the amplitude.

The E'' modulus of the aniline resin compound behaves differently. The amplitude dependence is less than it is in the other reinforced compounds. It must be assumed that the type of bonds which are here responsible for the E'' modulus are different from those involved in the other reinforced compounds.

INFLUENCE OF COMPOSITION

Finally Table IV shows to what degree changes in the composition of the natural-rubber compounds can influence the dynamic characteristics. The measurements were made at (1) two frequencies, viz., 20 and 100 cycles per sec. at 25° C; and (2) two temperatures, viz., 25° and 80° C at 70 cycles per sec. The amplitude was held constant at 0.5 per cent, the static compression at 2 per cent of the height of the rubber samples. The height h_0 and diameter D_0 were each 10 mm.

From Table IV the following conclusions can be drawn:

(1) The type of carbon black used in the rubber compound has a marked influence on the E' modulus. This modulus is high in the SAF and the EPC carbon black compounds and smaller in the HAF black compound. The loss factor, on the other hand, is approximately the same for all the carbon blacks tested.

(2) Where no carbon black was used as reinforcing filler the loss factor is slight. In the case of the light colored reinforcing filler Aerosil, this is to be attributed mainly to the high E' modulus. For the rubber-aniline resin compounds both components of the E modulus are small.

(3) The loss factor of compounds vulcanized with tetramethylthiuram disulfide (Thiuram) is nearly twice as great as that of comparable sulfur-containing compounds. These compounds show a very great internal heat development in the Goodrich flexometer.

SUMMARY

Since rubber articles are often exposed in service to small periodic deformations, great interest attaches to the dynamic-mechanical characteristics of rubber. It has been established that the conditions under which these characteristics are determined have a pronounced influence on the results obtained, so that the measurements must be undertaken under precisely specified conditions.

A new test apparatus is described for measuring the dynamic-mechanical characteristics, with which measurements can be performed at any desired stress setting, frequency, temperature, and amplitude on the same samples, both for compression and for shear loading.

The incompressibility of filler-free natural-rubber compounds has been demonstrated by measurements made on samples with different shape factors and with varied static initial stress, under compression and with shear loading.

The temperature, frequency, and amplitude dependence of the dynamic-mechanical characteristics of different rubber compounds is discussed on the basis of a number of measurements. The maximum value of the loss factor, which occurs in the vicinity of the second-order transition point, appears at a

higher temperature in GR-S (cold rubber), Vulkollan, and Butyl rubber than in natural rubber. There is a connection between this fact and the much greater frequency and temperature dependence of Butyl rubber compared to natural rubber in the vicinity of room temperature.

A compound based on natural rubber and a styrene-butadiene (85/15) copolymer shows two maxima in the loss factor. One of these is characteristic of natural rubber, the other of the polymer.

The dynamic characteristics of filler-free rubber compounds are not very sensitive to amplitude. It is found that the marked amplitude dependence of reinforced rubber compounds cannot be accounted for by increased temperature or by any nonlinearity of the stress-strain curve.

The influence of composition on the dynamic-mechanical characteristics of natural rubber has been tested for a number of compounds. It is established that the carbon black types can have a significant effect on the E' modulus. At small amplitudes the magnitude is greater for a compound containing SAF or EPC carbon black than for one containing HAF carbon black. Natural rubber reinforced with Aerosil or aniline resin shows a small loss factor, while compounds vulcanized with Thiuram show a large one.

The present study is part of a fundamental investigation on rubber carried out by the Research Division of the Rubber-Stichting in Delft under the direction of H. C. J. de Decker.

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RADIATION STABILITY OF ELASTOMERS *

C. D. BOPP AND O. SISMAN

SOLID STATE DIVISION, OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE

Data on how radiation affects plastics and elastomers show a rough relationship between radiation stability and Young's modulus¹. Generally, mineral-filled and rigid plastics are most stable, and natural rubber resists damage better than the synthetics. Addition of Butyl rubber, which softens when irradiated, to natural rubber, which hardens, gives a product with irradiated strength inferior to that of natural rubber.

ELASTOMERS

In Table I, the pre-irradiation mechanical behavior of elastomers is characterized by the breaking elongation and the dynamic Young's modulus. Resistance to damage is shown by the exposure required to decrease the elongation 50 per cent. From the similarity of radiation effects for the groups irradiated in air or in helium, it appears that the exact amount of air present is not significant for pieces as thick as these 0.1-inch tensile specimens.

Figure 1 shows that radiation affects the tensile strength and breaking elongation of an elastomer somewhat similarly, but breaking elongation is the more sensitive. Very roughly, the exposure for 10 per cent decreased elongation is one-fifth of the 50 per cent figure.

Natural rubber resists change best.—Table I shows that natural rubber has fivefold better radiation-damage resistance than the other elastomers. For Butyl rubber the exposure for 50 per cent decreased elongation is of the same order as for the other elastomers, but Butyl rubber becomes sticky and tarry. After the same exposure, the other elastomers, which are hardened as shown by Figure 2, may still be usable. For some purposes, natural rubber will withstand 10 times more exposure than will Butyl. Thiokol also becomes sticky, but at several-fold greater exposure than Butyl rubber. With these exceptions, all elastomers have the same order of stability, as is indicated by the tensile test.

Straining specimen during irradiation causes greater damage.—Crosslinking is predominant in elastomers that are hardened; cleavage, in those that are softened. For unstrained elastomers the net effect is given by the differences in the two processes; but if elastomers are irradiated while strained, the amount of recovery on removal of the stress may be decreased both by cleavage and crosslinking. To study the loss of recovery, cylindrical specimens were placed in the jig in Figure 3, compressed to $\frac{1}{4}$ inch, and irradiated. The recovery after removal from the jig is given in Table III.

The loss of recovery is sizable for exposures of an order of magnitude less than are required to decrease the breaking elongation appreciably. Either of two models may be postulated to explain this. The first model pictures both

* Reprinted, with omissions, from *Nucleonics*, Vol. 13, No. 7, pages 28-33, July 1955, and No. 10, pages 51-55, October 1955. The parts omitted comprise some experimental data and discussions on non-elastomeric plastics. In view of this, the title of the first paper has been modified from the original title of "Radiation Stability of Plastics and Elastomers."

TABLE I
 RADIATION STABILITY OF ELASTOMERS

Formulation	Energy absorption (rad/10 ³ nvt)	Breaking elongation		Initial value of dynamic Young's modulus (10 ⁸ dynes/cm. ²)
		Initial value (%)	Exposure for 50% decrease (10 ³ rad)	
Group I—Irradiated in air-filled containers *				
Natural rubber	0.6	420	0.5	2.3
Neoprene	2.5	450	0.06	—
Hycar OR	0.6	250	0.10	—
Butyl rubber	0.6	525	0.10	§
GR-S	0.6	270	0.10	1.8
Hycar PA	0.6	230	0.10	—
Thiokol 8T	0.4	162	0.10	—
Silastic 7-170	0.7	520	0.06	—
Group II—Irradiated in helium-filled containers †				
Polybutadiene	0.8	360	0.1	0.9
Hycar OR-15	0.8	320	0.1	1.2
Hycar OS-10	0.8	380	0.1	1.2
Neoprene GN	2.5	475	0.1	1.2
Thiokol	0.4	180	0.1	—
Silastic 250	0.7	320	0.1	4.0
Natural rubber	0.8	460	0.1	0.3
Hycar PA	0.8	660	0.05	0.6
Hypalon 82	2.5	250	0.1	3.0
Group III—Natural rubber with plasticizer ‡				
L.P. oil	0.8	560	0.1	0.33
Diocetyl phthalate	0.8	440	0.1	0.25
Diocetyl sebacate	0.8	520	0.1	0.30
Tributoxyethyl phosphate	0.8	440	0.1	0.47
TP90B	0.8	360	0.1	—
Plasticizer SC	0.8	390	0.1	—

* Formulations are given in Table 2.

† No attempt was made to remove final traces of air from containers. These materials have different cures and different formulations than Group I, but mostly contain the same base polymers.

‡ Exact composition are given by Bopp and Siaman³.

§ Durometer hardness decreases.

cleavage and crosslinking occurring together, but cleavage effects are masked by crosslinking in the absence of strain. In the presence of strain, cleavage and crosslinking no longer tend to cancel each other, but are additive. The second model pictures the occurrence of very little cleavage, but postulates greater

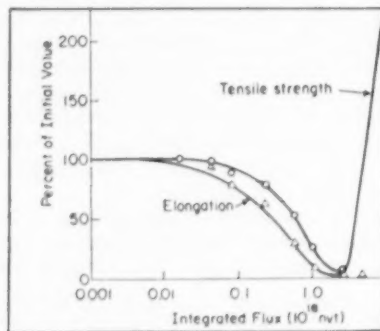


FIG. 1.—Radiation effects natural rubber's tensile strength and elongation in a roughly parallel manner. This is typical for elastomers. For natural rubber, 1 nvt is equivalent to 0.6×10^3 rad.

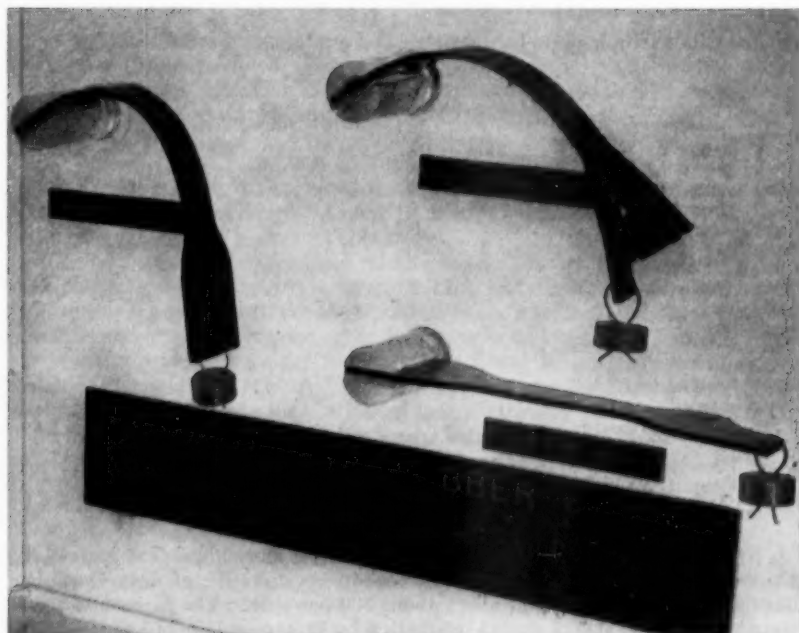


FIG. 2.—Natural rubber loses its elastomeric properties and becomes hard and brittle when irradiated.

crosslinking effects in the presence of strain, owing to the hindrance imposed upon the uncoiling of molecular segments that have become crosslinked in a strained configuration.

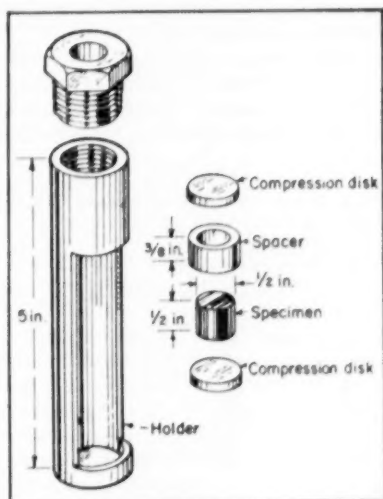


FIG. 3.—Jig used to compress samples listed in Table III.

TABLE II
FORMULATIONS OF GROUP I ELASTOMERS*

Components	Parts by weight						
	Natural rubber	Neoprene W	Hycar OR-15	GR-I Butyl	GR-S Styrene	Hycar PA-21	Thiokol ST
Base polymer	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5		0.5
SRF Black	70	45	55	75	70		60
Phenyl-2-naphthylamine	1	2					
Stearic acid	1	0.5		2		1	3
Sulfur	3		1.5	1.5	1.75	0.5	
Mercaptobenzothiazole	0.6			0.5			
Magnesium oxide		2					
Permalux		0.5					
Benzothiazolyl disulfide			1				
Tetramethylthiuram disulfide				1			
Santocure					1.5		
HMF (Phlblack O)						40	
Trimene base						3	
GMF (<i>p</i> -quinone dioxime)							1.5
Ca-10							2
Cure: Time (min.)	25	20	30	60	40	60	
Temp. (° F)	292	307	307	307	307	310	

* Chemical formulas have been given by Bopp and Sisman³.

Evidence that the first of the two models is the more important is given by x-ray diffraction measurement of the loss of crystallinity of natural rubber irradiated to 10^7 rad while strained about 300 per cent. The sample was protected from ozone attack during irradiation by an atmosphere of helium. The loss in crystallinity is even more sensitive to irradiation than is the loss of recovery. Since the amount of crosslinking for this low exposure is too small to affect the mechanical properties of unstrained elastomers, it is believed that the loss of crystallinity results largely from cleavage-induced stress relaxation. To further study cleavage, it is planned to measure creep during irradiation.

Adding antioxidants and mineral fillers yields no improvement.—Almost all rubber formulations contain small amounts of stabilizers or antioxidants that protect the rubber by absorbing energy that would otherwise damage the polymer. Special formulations shown in Table IV were made for testing the possibility that relatively large amounts of antioxidant might afford protection against radiation. Also, an attempt was made to improve the radiation stabil-

TABLE III
PERCENTAGE RECOVERY OF ELASTOMERS COMPRESSED
25 PER CENT DURING IRRADIATION

Elastomer*	In jig 190 hours		In jig 840 hours	
	Unirradiated	Irradiated† 0.03×10^{18} nvt	Unirradiated	Irradiated† 0.16×10^{18} nvt
Natural rubber	93	52	90	25
GR-S	90	53	88	22
GR-I	91	23	88	Tarry fluid
Neoprene W	62	20	42	
Hycar OR-15	92	62	90	
Hycar PA-21	92	58	91	24
Silastic	97	27	95	14
Thiokol ST	90	2	82	0

* Compositions are given in Table II.

† For Neoprene, 1 nvt $\sim 2.5 \times 10^{-3}$ rad; for Thiokol, 1 nvt $\sim 0.4 \times 10^{-3}$ rad; for the others, 1 nvt $\sim 0.6 \times 10^{-3}$ rad.

ity of natural rubber by including large amounts of mineral filler in the recipe, since certain mineral-filled plastics are very resistant³. No improvement in retention of either breaking elongation or breaking strength was realized for any of these formulations over the formulations of Table II.

Compounding Butyl with natural rubber gives product inferior to natural rubber.—Since natural rubber is hardened by irradiation, while Butyl rubber is softened, it was thought that compounding the two polymers would result in a mixture that might be more resistant than either alone. Four mixtures were tried—the recipes are given in Table IV.

The mixtures all decrease more rapidly in breaking strength and elongation than natural rubber, which is more stable than Butyl rubber. But the change of hardness is less for both the 50:50 mixtures and the 25:75 mixtures than for natural rubber. This constancy of hardness is believed to result from the combined effects of cleavage, which softens Butyl rubber, and crosslinking, which hardens natural rubber. For most applications the constancy of hardness will not compensate for the loss of tensile strength and elongation; thus, no net improvement over natural rubber is achieved by the mixtures.

TABLE IV
EIGHT SPECIALLY COMPOUNDED ELASTOMERS*

Ingredients	Parts by weight							
	1	2	3	4	5	6	7	8
Natural rubber	100	50	25	10	100	100		100
Neoprene W							100	
Butyl rubber		50	75	90				
Butyl reclaim					60			
Asbestos fiber	250							
Dodecanethiol						10	10	
SRF black		70	70	70	70	70	40	70
Dibutyltin dilaurate								10
Calcium silicate		10	10	10				

* Complete formulations are given by Bopp and Sisman².

TEST CONDITIONS

When compared on the basis of the energy absorbed, all types of high-energy radiation produce approximately similar effects on materials in which excitation and ionization are highly efficient in producing chemical reactions. To establish the validity of this observation, it is necessary to know the irradiation conditions.

Irradiation.—Most of the materials were exposed in the high-flux region of the ORNL Graphite Reactor in a water-cooled (25–40° C) channel, but some irradiations were made with Co⁶⁰ and Au¹⁹⁸ sources. The maximum gamma source exposure⁴ was 10⁹ rad; the maximum reactor exposure was 3 × 10¹⁰ rad.

In calculating the energy absorbed by samples in the reactor, it is generally necessary to consider fast neutrons, gammas, and secondary radiation from thermal-neutron-absorption reactions. The secondary radiation is appreciable only for elements with absorption cross-sections much larger than those of either carbon or hydrogen; and it is less important for these specimens that are thin with respect to gamma absorption than it is for other geometries.

The combined high-energy radiation in the reactor amounts to about 10⁶ rad/hr. The ratio of fluxes of thermal neutrons (< 1/30 ev), epithermal neutrons (1/30 ev to 1 Mev), fast neutrons (> 1 Mev), and gammas (assuming 1

Mev average energy), is 1.0:0.6:0.04:0.5, respectively. When the integrated flux is expressed in nvt, it means the number of thermal neutrons that have passed through 1 cm².

Correlation of damage and energy absorbed.—Approximately equivalent changes were produced by both the reactor and gamma sources for equal energy absorption. This is not surprising since the ionization and excitation processes are similar for all types of high-energy radiation.

The term high-energy radiation is used here to include gamma and beta radiation, fast neutrons, and charged particles of all types. With fast neutrons, excitation and ionization are produced indirectly through protons ejected in collisions of fast neutrons with hydrogen atoms. The other types of high-energy radiation may cause ionization and excitation directly.

The efficiency of radiation in producing chemical reactions in materials is determined by the chemical structure of the material. Many inorganic materials are not changed greatly by gamma or beta radiation, but only by the heavier particles that produce displaced atoms. Most organic materials are changed largely by excitation and ionization. The amount of energy absorbed by ionization and excitation is generally much greater than that absorbed in displacing atoms, and often the latter may be neglected for materials damaged by ionization and excitation⁶.

The energy-absorption approximation for polymers has been tested experimentally² for mechanical property changes that occur for exposures up to 10⁹ rad. In the intensity range 10⁶–10⁷ rad/hour, agreement between gamma sources and the reactor (with mixed gamma and fast-neutron radiation) was found within about a factor of two, but comparison was possible only for the more radiation-sensitive materials. Another indication of the validity of the energy-absorption approximation was obtained when plastics were irradiated in the reactor, both enclosed in cadmium and without the cadmium³. The increase of the gamma flux due to the (n, γ) reaction on the cadmium was found to increase the radiation-induced change in proportion to the additional energy absorbed.

In the high-flux region of the ORNL Graphite Reactor, the energy absorption for materials composed entirely of carbon and hydrogen is given approximately by: $R = (4.8C + 0.31)N \times 10^{-2}$; where R = energy absorbed, rad; C = weight percentage of hydrogen; N = thermal neutron exposure, neutrons/cm². If elements in addition to carbon and hydrogen are present, the applicability of this relation is determined largely by the thermal-neutron-absorption cross-sections and the decay schemes of the additional elements. For hydrogen and carbon the energy absorption due to thermal neutrons is small enough to be negligible. For elements with high cross-sections, and especially those that do not go to stable elements, additional energy will be absorbed from the gammas and betas emitted in the absorption process and from the recoil of the atoms on emitting radiation.

For the elastomers in Table I that contain elements with high thermal-neutron-absorption cross-section, the rad/nvt values were obtained by comparing changes produced in the reactor with those produced in gamma sources.

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HOW RADIATION CHANGES MECHANICAL PROPERTIES OF POLYMERS

High-energy radiation alters the molecular structure of elastomers by crosslinking and cleavage—chemical changes. Consideration of the mechanisms of deformation explains how these chemical changes affect the mechanical properties.

RADIATION EFFECTS

All elastomers tested were hardened by crosslinking with the exception of Butyl rubber and Thiokol, which were softened by cleavage. Sensitive properties of crosslinked elastomers are tensile strength and breaking elongation as well as hardness. For cleaved elastomers, the compression set is a very sensitive property. The stress relaxation of elastomers that are strained during irradiation is very sensitive for both groups.

DEFORMATION MECHANISMS

High-polymer molecules are in the form of linear chains, which are sometimes crosslinked to a three-dimensional network. Elastomers differ from plastics in having weaker van der Waals forces. In plastics, the forces are strong enough to maintain the solid state in the absence of stress. In elastomers, the forces are weak as in a liquid, and the solid state is maintained only by a few primary-valence crosslinks that form a loose network.

It is convenient to consider two mechanisms of deformation, *ordinary elasticity* and *high elasticity*¹. For polymers, it is customary to express ordinary elasticity in terms² of a spectrum of retardation times, τ .

It is rarely possible to fit experimental data with only one value of τ , so it is customary to use a smooth distribution of values. The distribution of retardation times is often sensitive to the rate of dissipation of frictional energy³ and thus may depend on the specimen's dimensions. On the other hand, the free volume⁴ may be important, and for this reason distribution of retardation times is usually sensitive to temperature.

A qualitative explanation of how radiation affects the mechanical properties of high polymers is given by considering only two processes—crosslinking and cleavage. The effect of crosslinking is to tend to impede viscous flow, and to increase the retardation times. The equilibrium value of Young's modulus for high elasticity is given by the kinetic theory as directly proportional to the concentration of crosslinks⁵.

$$E = AkT/V \quad (1)$$

Measured values of dynamic Young's modulus for certain elastomers may not approach very closely the equilibrium value.

Cleavage has the effect of reducing the yield stress for viscous flow. The equilibrium value of Young's modulus for high elasticity is decreased by cleavage, since the number of crosslinks is reduced. The retardation times for plastics not initially crosslinked are often not changed much by cleavage.

Materials usually exhibit more than one deformation mechanism⁶, and the relative prominence depends on the strength of the van der Waals forces (on the chemical structure), on the amount of crosslinking (a large amount of crosslinking tends to impede viscous flow and high elasticity), and on the temperature. This discussion is limited to room temperature (25° C).

Crosslinking of elastomers is typified by the tensile curves of natural rubber, as shown in Figure 1. Before irradiation, the deformation is mostly by high elasticity. After long irradiation, natural rubber acquires a rigidity comparable with that of glasses—so care must be exerted in handling to avoid breaking specimens.

Young's modulus may be decreased by irradiation for some polymers but increased for others. This is explained by the differences in the relative prominence of the crosslinking and cleavage processes for different polymers. For natural rubber, the predominant radiation effect is crosslinking; for Butyl rubber, it is cleavage.

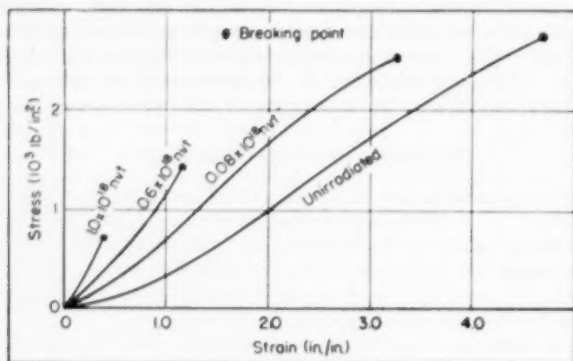


FIG. 1.—Stress-strain curves for reactor-irradiated Natural Rubber.
1 nvt is equivalent to 0.6×10^{18} rad.

DEFINITIONS

High elasticity is confined to idealized elastomers in which the only mechanism for deformation is the uncoiling of molecular segments, and in which the restoring force results entirely from thermal motion of the molecular segments.

Ordinary elasticity is that involved with actual elastomers or plastics.

Viscous flow describes the liquid-like state that solids may assume under stress.

A = a constant of the order⁶ of 1.

c = the rate constant.

E = equilibrium value of Young's modulus for *high elasticity*.

ΔE = increase of dynamic Young's modulus.

ΔE_{∞} = limiting increase for long exposure.

k = Boltzmann's constant.

n = a parameter ≥ 1 .

R = exposure.

T = absolute temperature.

U = energy to produce a crosslink, electron volts.

V = volume per crosslink.

ΔV = decrease of specific volume.

ΔV_{∞} = limiting volume decrease that is approached at long exposure.

y = deformation at time t after application of stress.

y_0 = equilibrium value of deformation resulting from y .

ρ = density.

τ = retardation time; defined by: $y = y_0(1 - e^{-t/\tau})$.

5.22×10^{22} = ev/rad.

CROSSLINKING PROCESS

The rate of the volume change that accompanies the cooling of a high polymer becomes so slow at the second-order transition temperature that it introduces a discontinuity in the specific volume-temperature relation as it is ordinarily measured. Perhaps if a sufficiently long waiting period were allowed between changing the temperature and measuring the volume, the volume-temperature relation would be continuous to absolute zero.

Analogously, the rate of crosslinking may be diffusion controlled, since hydrogen diffuses out of the polymer during crosslinking, and the molecular segments diffuse closer together—as is evidenced by hydrogen evolution and decreased specific volume⁶.

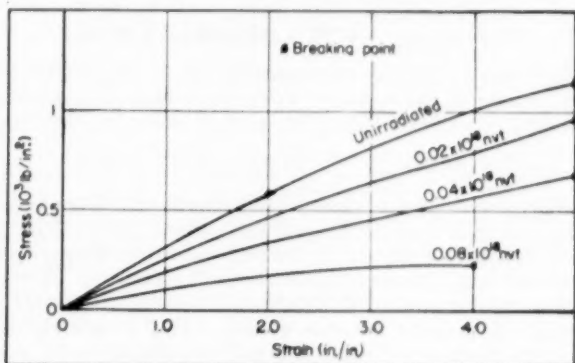


FIG. 2.—Stress-strain curves for reactor-irradiated Butyl Rubber GR-I-50.
1 nvt is equivalent to 0.6×10^{18} rad.

If it is postulated that crosslinking results when activated molecular segments diffuse together, then crosslinking is proportional both to the concentration of activated molecular segments and to the rate of diffusion. Suppose there exists an upper limit on the number of molecular segments that it is possible to activate. When the intensity of the radiation field is increased sufficiently for this upper limit to be approached, the rate of crosslinking will become independent of intensity. Thus, the energy absorption approximation⁷ can no longer hold. It appears that this condition will be approached at a lower intensity for the more rigid materials because the limiting value of the steady-state concentration of activated molecular segments will likely be approached at a lower intensity, since the rate of deactivation by the crosslinking process is less. This suggestion is intended as a caution that, although the energy absorption approximation has been tested experimentally for nonrigid materials, it should not be assumed for very rigid materials without experimental confirmation. In the intensity range 10^6 – 10^7 rad/hr, there was observed only a small intensity dependence for many nonrigid materials.

The sensitivity of Young's modulus to crosslinking for ordinary elasticity has been explained in terms of increased retardation times. To explain the

nearly constant rate of crosslinking (though the retardation times are increased), it is necessary to postulate that crosslinking does not microscopically restrict the diffusion of neighboring molecular segments except perhaps very close to crosslinking sites. The effect on the retardation times must then be largely caused by the formation of a network structure. Thus, it is possible for the macroscopic retardation times to be affected by crosslinking without affecting the microscopic diffusion rate of a large portion of the molecular segments.

From these considerations it appears necessary to restrict the correlation between rigidity, measured by the Young's modulus, and the rate of crosslinking to noncrosslinked polymers. Even in the absence of crosslinking, the correlation is only an approximation, since the microscopic rate of diffusion may be only roughly inferred by using Young's modulus to estimate the strength of the van der Waals forces.

The rate of crosslinking for some elastomers is nearly constant in the early stages of crosslinking, but later drops off rapidly. The decrease of specific volume may be fitted to the equation:

$$\Delta V = \Delta V_{\infty}(1 - e^{-cR}) \approx \Delta V_{\infty}(cR), \quad \text{if } cR \ll 1 \quad (2)$$

The dynamic Young's modulus was measured for several elastomer formulations⁸. The increase of the dynamic Young's modulus at room temperature and in the frequency range 10–100 cycles/sec is given by the empirical relation:

$$\Delta E = \Delta E_{\infty}(1 - e^{-cR})^n \approx \Delta E_{\infty}(cR)^n, \quad \text{if } cR \ll 1 \quad (3)$$

Roughly the same value of c is given for Neoprene-GN either by the changes in the specific volume or the Young's modulus. For Hycar-OR, a higher value of c is found for Equation 3 than for Equation 2. Only for these two elastomers were sufficient data available to estimate c by both equations. Neoprene has a higher effective exposure owing to its chlorine content; Hycar-OR reaches a saturation value of Young's modulus quickly owing to a high value for n . The agreement in the case of Neoprene is taken as characteristic of elastomers with n less than 4; the lack of agreement of Hycar-OR is associated with the high n value.

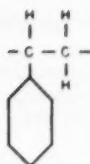
According to the kinetic theory of high elasticity, Young's modulus should vary approximately in proportion to the concentration of crosslinks, although the situation is complicated by the "entanglement factor"⁹. The experimental results indicate proportionality to the n th power of the concentration of crosslinks, where $n \geq 1$. Perhaps additional weight over that predicted by the kinetic theory is given to crosslinking, owing to increased retardation times. Disregarding the entanglement factor, the energy required to produce a crosslink may be calculated from⁸:

$$U = 5.22 \times 10^{23} \rho A k T / (c^n \Delta E_{\infty})^{1/n} \quad (4)$$

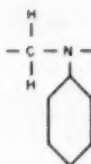
For the plasticized natural rubber formulations⁸, Equation 4 gives about 20 electron volts per crosslink, which is of the same order as given by swelling measurements for crepe rubber¹⁰.

CLEAVAGE PROCESS

That crosslinking is the predominant radiation-induced process for many liquid hydrocarbons is evidenced by the viscosity change. Because of the similarity between elastomers and liquids, it is not surprising that many elastomers also are hardened by irradiation. As discussed, the rate of crosslinking is



The repeating unit in the structural formula of polystyrene, which is the most stable of the unfilled polymers tested.



The repeating unit of aniline-formaldehyde polymer. As for polystyrene, stability is attributed to the bulky side groups containing a benzene ring.



Present in many elastomers; since the stability of elastomer appears to be insensitive to the amount of unsaturation, this group is ranked with next group.



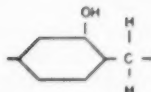
The repeating unit of polyethylene.



Present in Nylon, which shows the same order of stability as polyethylene.



The repeating unit of silicone rubber, which shows the same order of stability as most other elastomers.



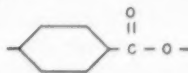
The repeating unit of phenol-formaldehyde polymer. The benzene ring in main chain is thought to increase cleavage, since unfilled phenolic crumbles for exposure that do not decrease strength of polyethylene (this contrasts with effect of benzene ring in polystyrene, in which it is in a side group).



Also taken to be less stable than polyethylene. Polyallyl diglycol carbonate, polyvinyl formal, and polyvinyl butyral are softened. Selectron-5038 is hardened; however, this plastic is initially very soft and shows a high rate of crosslinking.



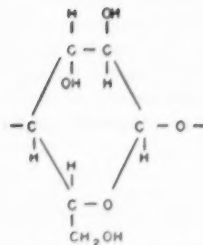
Present in Thiokol, for which a balancing of cleavage against crosslinking causes small hardness change, but decreases the ultimate strength.



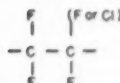
Present in Dacron. The predominant radiation change is embrittlement.



Present in polyvinyl chloride. Unplasticized polyvinyl chloride is softened by cleavage, though highly plasticized forms are hardened.



The repeating unit of cellulose. Rapid embrittlement of cellulosic plastics shows that this structure is sensitive to chain cleavage.



The repeating unit of Teflon and fluorothene, which become brittle and crumble apart at relatively short exposure. Resistance to cleavage is poor.



The repeating unit in polymers with quaternary carbon atoms: polymethyl methacrylate, Butyl rubber, and poly- α -methylstyrene.

Fig. 3.—Polymer groups ranked in order of their stability against cleavage. In addition to the four groups which are present in the various elastomers, other groups present in various plastics are included in this order of stability to show the interrelation of the chemical structures of elastomer and plastics with respect to this property.

less for rigid materials. But, from Figure 3 it is apparent that cleavage outweighs crosslinking for some materials.

Certain moderately rigid materials that have a low rate of crosslinking are also very resistant to cleavage. Other materials of the same rigidity show much less resistance to cleavage. It appears that rigidity will not appreciably retard cleavage of moderately rigid materials.

Figure 3 lists the chemical groupings of some polymers previously discussed⁴ in order of stability against cleavage. The rankings in Figure 3 are not precise with regard to some of the groupings that fall close together, but a very large difference in stability may exist between those spaced far apart. The manner in which the ranking was obtained is given in Figure 3.

There is very little experimental data on the mechanism of cleavage in solid high polymers. There is insufficient data for a very complete picture, but a simple concept is that atomic hydrogen, fluorine, and such, can react in some instances to break the main polymer chain.

The evolution of hydrogen gas indicates that atomic hydrogen is at some time present in irradiated solid high polymers. Similarly, the hydrogen halides are evolved by halogen-containing materials. If these atoms that are not part of the main chain are released, cleavage may occur as a possible consequence if they react with atoms in the polymer chains. The low ranking of the ethers, the thioethers, and the quaternary carbon atom may indicate a high efficiency of atomic hydrogen in these cases. A rearrangement mechanism has been proposed that otherwise accounts for the low stability of the latter grouping¹¹.

SUMMARY

Ordinary elasticity, high elasticity, and viscous flow are the mechanisms of deformation of solid polymers. Qualitatively, the effect of radiation on the mechanical properties of polymers can be described by considering the effect of crosslinking and cleavage on these mechanisms. Crosslinking tends to impede viscous flow. The equilibrium value of Young's modulus for high elasticity is directly proportional to the concentration of crosslinks, but for ordinary elasticity the sensitivity of Young's modulus is less for more rigid materials. Cleavage reduces the yield stress for viscous flow, and decreases the equilibrium value of Young's modulus for high elasticity. Young's modulus for ordinary elasticity is again insensitive for the more rigid materials.

The changes in the mechanical properties of irradiated elastomers depend on the rates of crosslinking and cleavage. These rates are governed both by the polymer's chemical structure and by the strength of the van der Waals forces. For uncrosslinked polymers, the change of Young's modulus is a measure of the crosslinking rate in the case of less rigid materials. Sensitivity to chain cleavage has been correlated with chemical structure for the materials studied.

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A STUDY OF THE AGING OF NATURAL RUBBER BY MEANS OF INFRARED SPECTROSCOPY V. AGING ACCELERATED BY HEAT *

VOJTECH KELLÖ, ALEXANDER TRÁČ, AND JOLANA HRIVÍKOVÁ

DEPARTMENT OF PHYSICAL CHEMISTRY OF THE SLOVAK TECHNICAL UNIVERSITY,
BRATISLAVA, CZECHOSLOVAKIA

INTRODUCTION

In foregoing work¹ we studied the light aging of natural rubber, using infrared spectroscopy as the technique of investigation. The results show that during aging in light two simultaneous processes are going on in natural rubber, e.g., degradation and spatial crosslinking². In this the effects of light and heat were found to be different³. To clarify this problem a more detailed study limited only to the influence of heat alone (in darkness) seemed necessary. Aging accelerated by heat was first studied quantitatively by means of infrared spectroscopy by D'Or and Kössler⁴. They have presented a formal kinetics of the oxidation of rubber on the basis of the Semenov theory of chain reactions with degenerated branching and have shown that, in accord with this theory, it is possible to express the number of oxidized groups by the equation: $n = C \cdot e^{\varphi t}$, where n is the amount of oxidized groups proportional to the extinction of the absorption band of the respective group, t is time and C and φ are constants. However, it was necessary to complete and extend this work in many respects.

EXPERIMENTAL PART

The equipment used, the preparation of samples, and the experimental technique were described in previous articles⁵, dealing mainly with photocatalytic aging.

In studying heat aging we have based our observations in principle on the time course of the growth of extinction of absorption bands pertinent to the groups C=O (5.79 μ) and O—H (2.86 μ), which develop as a result of oxidation. The kinetic curves obtained have a characteristic S-shape. Following a certain induction period a steep ascent takes place which, however, ceases after a certain time.

Whereas the quantitative spectroscopic measurement of light aging is well reproducible, considerable difficulties are encountered in the heat aging of natural rubber at elevated temperatures. We have, therefore, studied in detail the conditions under which reproducibility of measurements may be assured. Here we shall limit ourselves to some results of our study leading to the definition of optimum conditions of reproducibility. While a solid film, prepared in the customary way⁶ from a benzene sol of natural rubber, is perfectly uniform, it becomes non-homogeneous during aging above 80° C. This of course excludes a quantitative spectroscopic measurement. Besides, the process of

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heat aging is extremely sensitive to direct contact of the sample with metals, or substances containing antioxidants (vulcanized rubber), as well as to an atmosphere containing traces of substances which may influence the chain-linkage mechanism of oxidation of natural rubber. This influence is effective at considerable distance from the point of contact of the said substances with the rubber film. A good reproducibility requires under all circumstances a perfect (several months') extraction of the rubber sample in a methanol-acetone mixture. This is evidence of nonhomogeneity of the natural rubber itself which is not eliminated even by dissolving in benzene. Therefore, the natural components of rubber must be linked by intermolecular bonds which can be attacked only by extraction with a polar solvent. The transition of the elastic form of rubber into the plastic form⁷ around 80° C helps to increase the diffusibility of

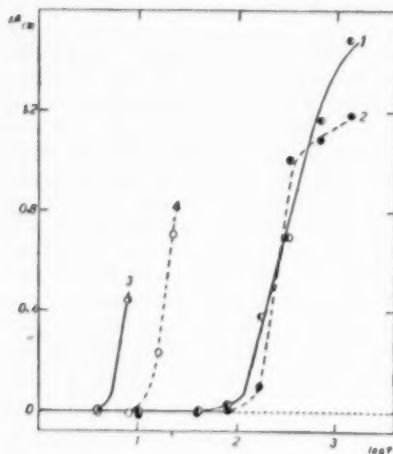


FIG. 1.—Time course of the growth of extinction for C=O groups. 1. 120° C (0.800), 7 films; 2. 120° C, (0.820); 3 and 4. 160° C (0.840). Test — uninterrupted, - - - interrupted; Extracted sample II; t = time in minutes.

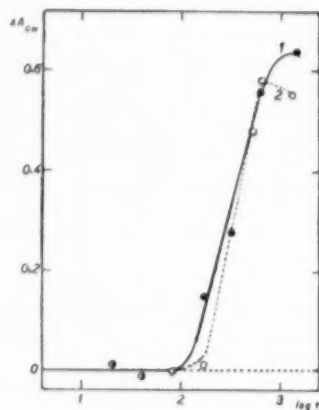


FIG. 2.—Time course of growth of extinction for O—H groups. 1. 120° C (0.800), 7 films; 2. 120° C (0.820). Test — uninterrupted, - - - interrupted; Extracted sample II; t = time in minutes.

ingredients. Besides, above this temperature, the thickness of the film may change, due to softening of the sample. It is, therefore, necessary to maintain the samples in a strictly horizontal position at higher temperatures.

The time process of the influence of heat on samples can be followed basically by two methods. Experimentally the simpler method is to study the aging on one film wherein the action of heat is interrupted at regular time intervals to make the spectroscopic measurements. Because the repeated interruptions of the reaction influence its chain mechanism, it is in principle more correct to follow the course of the reaction without interruption. This requires a larger number of perfectly identical rubber films which are simultaneously exposed to the action of elevated temperatures. In adequate time intervals individual films are taken one after another for quantitative spectroscopic investigation of changes in absorption bands of certain groups which indicate changes in structure. The number of films is usually 8 to 10, depending on the number of determinations necessary for the construction of kinetic curves. The shape of

the kinetic curves for the C=O and O—H groups is almost equal in both procedures; only in the range above 120° C are there marked differences, especially in the length of induction period (Figures 1 and 2). This points to an efficient termination of reaction chains as a consequence of the lowering of the temperature at the interruption. As may be seen from the figures, the fluctuation of the experimentally found points in the second procedure is compara-

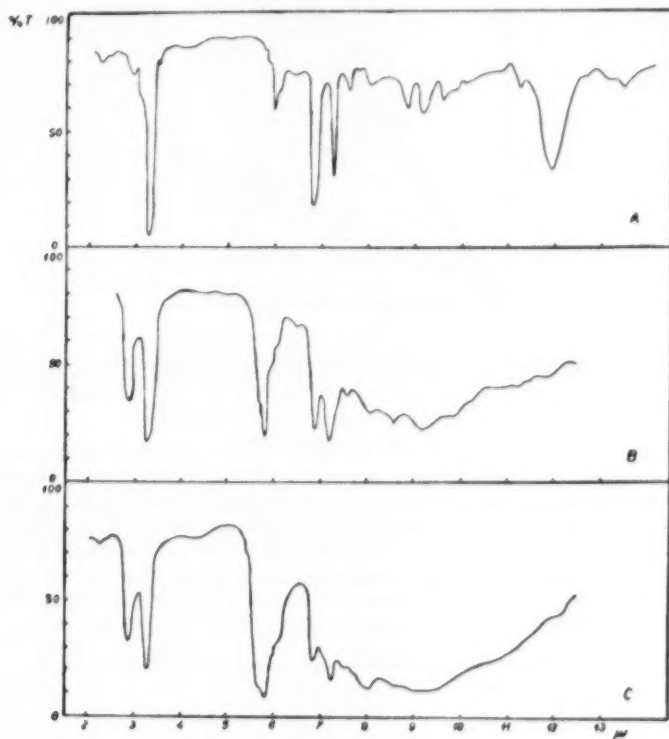


Fig. 3.—Infrared absorption spectra. A. Natural rubber (white crepe) extracted; B. Natural rubber extracted and irradiated by a mercury lamp at 14 cm. for 1600 minutes at 35° C; C. Natural rubber extracted and kept for 2400 minutes at 125° C in darkness.

tively small, and this indicates the correctness and good reproducibility of this new technique. This method was made practicable by a rotational method of the preparation of the films⁶.

RESULTS AND DISCUSSION

CHANGES IN THE SPECTRUM

The changes found in the infrared absorption spectrum of rubber during heat aging are in agreement with up-to-date literature⁸. In contrast to the changes during photocatalytic aging, the main difference is seen in a generally more marked increase of extinction of the absorption band at 5.65 μ pertaining

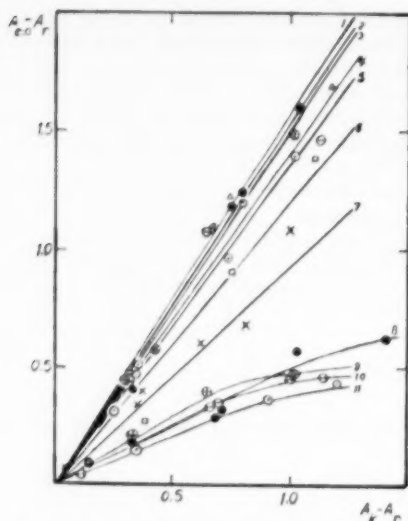


Fig. 4.—Dependence of degree of oxidation on thickness of sample at different temperatures. Number of C=O groups after reaching the stationary section as a function of the extinction of the control band. Temperature: 1. Δ 160, 2. \bullet 150, 3. \oplus 140, 4. \ominus 130, 5. \circ 120, 6. \square 110, 7. \times 60, 8. \bullet 100, 9. \oplus 90, 10. \ominus 80, 11. \circ 70° C. Extracted sample II.

to C=O groups in ester or carboxyl linkages. Their growth is apparent by a marked widening of the C=O band, already noticeable from the middle of the steep ascending part of the kinetic curves, while in the case of light aging the widening of the band is observable only as the reaction curves pass to the final stationary section. This also corresponds to a broad absorption in the area 7.5–11 μ , indicating substantial changes in the original structure of natural rubber during heat aging. The bands at 6 and 6.1 μ , pertaining to double bonds, remain visible even after extensive destruction (Figure 3).

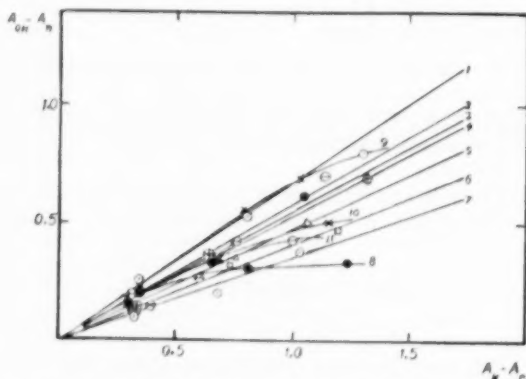


Fig. 5.—Dependence of degree of oxidation on thickness of sample at different temperatures. Amount of O—H groups after reaching the stationary section as a function of the extinction of the control band. Temperature: 1. \times 120, 2. \bullet 140, 3. \oplus 130, 4. \ominus 110, 5. Δ 150, 6. \square 160, 7. \circ 100, 8. \bullet 70, 9. \oplus 60, 10. \times 80, 11. \ominus 90° C. Extracted sample II.

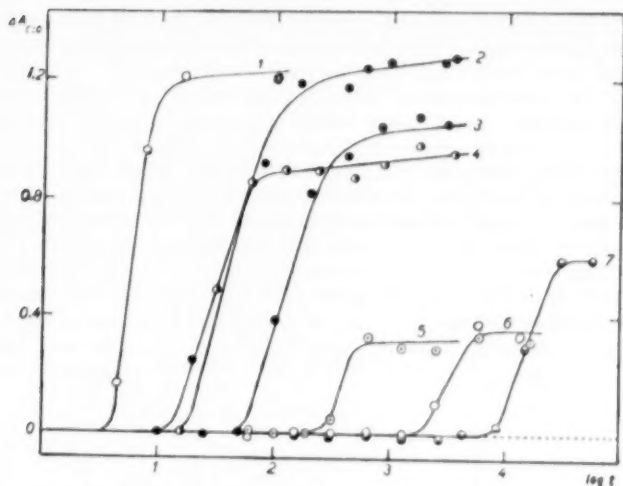


Fig. 6.—Dependence of growth of extinction of absorption band for C=O groups on time at temperatures 60–160°C. 1. 160°C, (0.700); 2. 150°C, (0.810); 3. 120°C, (0.758); 4. 140°C, (0.782); 5. 100°C, (0.714); 6. 80°C, (0.700); 7. 60°C, (0.636). Extracted sample I; t = time in minutes.

DEPENDENCE OF THE OXIDATION PROCESS ON THICKNESS OF THE SAMPLE

Whereas the light aging exhibits a marked surface character⁹, heat aging shows a somewhat more complicated picture. The dependence of the course of oxidation on the thickness of the sample was determined from the ratio of the

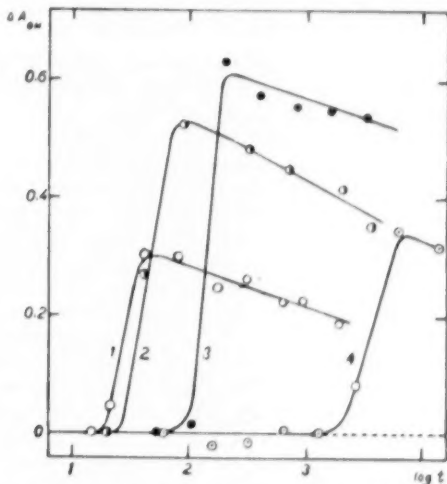


Fig. 7.—Dependence of growth of extinction of absorption band for O—H groups on time at temperatures 60–160°C. 1. 150°C, (0.650); 2. 140°C, (0.782); 3. 120°C, (0.758); 4. 80°C, (0.700). Extracted sample I; t = time in minutes.

numbers of C=O and O—H groups, after attaining the final stationary zone of the kinetic curves, to the thickness of the film. The numbers of C=O and O—H groups were expressed by the respective extinctions and the thickness of the film by the extinction of the control band (7.26μ)¹⁰. The extinctions were in all cases corrected for light dispersion. Figure 4 shows the dependence of extinction of the C=O groups on the extinction of the control band in the temperature range of 60–160° C. Figure 5 shows this dependence for the O—H groups. As is evident from these diagrams, oxidation proceeds uniformly in the whole mass of sample at temperatures above 100° C, whereas at lower temperatures the reaction shows to some extent a surface character. This phenomenon may be related either to an increase of the diffusion velocity of oxygen in the sample with increasing temperature or perhaps to the unsaturated character of the rubber surface.

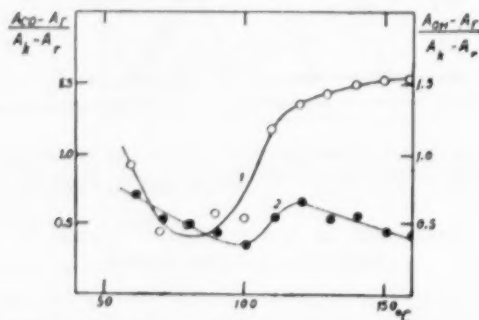


FIG. 8.—Temperature dependence of values denoting the initial course of curves represented in Figures 6 and 7. 1. Carbonyl groups. 2. Hydroxyl groups. Extracted sample II.

TIME COURSE OF OXIDATION

Figures 6 and 7 show the relationships between extinction of the absorption band for the C=O and O—H groups and time at temperatures 60–160° C. The thickness of all samples was practically equal ($A_{\text{control}} = 0.750\text{--}0.800$). The induction periods are shortened with temperature in both instances. However, while the curves of extinction growth for the carbonyl groups exhibit a stationary course after attaining a maximum, the curves for hydroxyl groups, after having reached a maximum value of extinction, start a gradual downward course. This is in agreement with the observations of D'Or and Kössler⁸. As is seen from the diagrams, the heights of the stationary zones are a function of the temperature. This is of basic importance for the solution of the mechanism of aging, since it indicates different numbers of active centers at different temperatures. In order to diminish as far as possible the influence of a surface effect at lower temperatures in evaluating the degree of oxidation, we have plotted (Figure 8) the temperature dependence of the initial course of the curve expressing the relationship between $A_{\text{C=O}}$ and $A_{\text{O-H}}$ in the stationary zones of the curves and the thickness (Figures 4 and 5). The diagrams of the relation between the heights of stationary sections and temperature show a minimum in the area of 75–95° C, which obviously corresponds to a change of the colloidal nature of rubber at the transition point, i.e., from the elastic to the plastic form. An analogy is the change of plasticity of rubber with temperature dur-

ing the milling operation, as observed by Busse and Cunningham¹¹. This dependence, in the case of non-extracted natural rubber shows a characteristic minimum in the area of 100–120° C (depending on the concentration of oxygen). According to Houwink¹² a combined effect of mechanical tear and oxidative degradation is instrumental in this case. There is the possibility of steric hindrance during the access of oxygen, because the rubber molecules are highly coiled and the mechanical working has a straightening effect. Based on our results it may be assumed that the lower degree of oxidation in a certain range of temperatures is the result of three simultaneously acting factors: 1. Formation of free radicals, the number of which suddenly increases during the thermal disaggregation of rubber in the transition of gel rubber into sol rubber (change from the elastic to the plastic form). 2. Increased reactivity of oxygen at higher temperatures. 3. Termination of chains, leading to a build-up of the original structure of rubber which had been degraded during coagulation and mechanical processing.

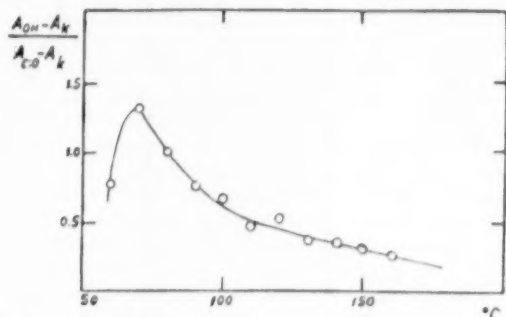


Fig. 9.—Ratio of amounts of C=O and O—H groups in stationary region as a function of the temperature, expressed as ratio of extinctions of their absorption bands.

The ratio of the amounts of C=O and O—H groups in the stationary zone drops with increasing temperature after an initial ascent (Figure 9). It is generally agreed¹³ that the oxidation of rubber to carbonyl groups proceeds through intermediary hydroperoxidic groups, the absorption band of which overlaps the band of O—H groups⁹. The decrease of hydroxyl groups with time after having reached a maximum, as well as a decrease of the ratio of their number to the number of carbonyl groups with time indicate that this change has been caused by transformation of hydroperoxidic into carbonyl groups. We assume that the velocity of disintegration of peroxidic groups increases with temperature. However, it cannot be excluded that ether linkages may be formed according to the scheme: $R-OH + HO-R' \rightarrow R-O-R' + H_2O$.

As far as changes in the number of double bonds are concerned, which have their absorption bands at 6 and 6.1 μ , these cannot be followed quantitatively at higher temperatures because of overlapping by the fast growing neighboring band of the C=O groups (5.8 μ). Only at temperatures below 80° C could we observe a moderate growth of double bonds during the induction period.

COMPUTATION OF ACTIVATION ENERGY

The kinetic study of the temperature dependence of the oxidation of rubber enabled us to determine its effective activation energy. As was pointed out by

D'Or and Kössler, the kinetics of thermal oxidation of rubber proceeds in the initial stage according to an equation derived by Semenov¹⁴ for nonstationary processes of oxidation of hydrocarbons, developing gradually with the time. In the simplest case, the velocity v of such processes, which Semenov calls de-generated, can be described by the equation:

$$v = v_0 \cdot e^{\varphi t} \quad (1)$$

where v_0 and φ are constants and t is time. The velocity constant φ is given by all constants of the elementary processes which characterize the probability

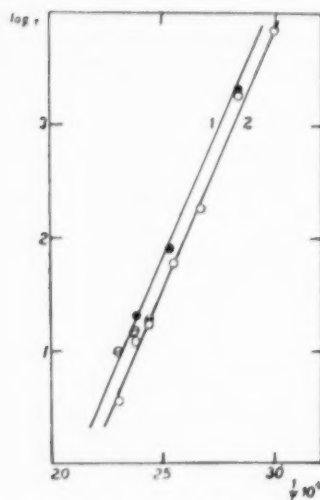


FIG. 10.—Dependence of $\log \tau$ on the inverse value of the absolute temperature for C=O and O—H groups. τ = length of induction period in minutes; Test ——— uninterrupted, - - - - - interrupted. Extracted Sample I.

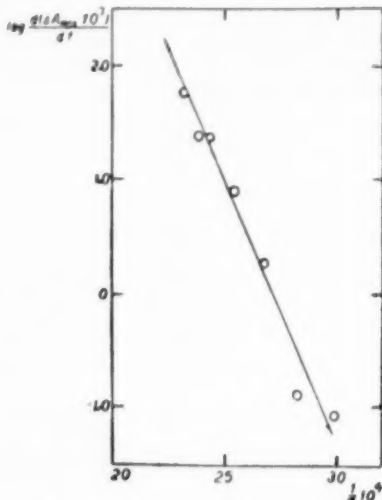


FIG. 11.—Dependence of maximum oxidation velocity v_{\max} , expressed by the increase of C=O groups, on the inverse value of the absolute temperature: $v_{\max} = [d(\Delta A)/dt]_{\max}$; Extracted sample I.

of branching and extinction of the active centers. Its relationship to the absolute temperature T can be expressed, at a constant pressure of oxygen, by the equation:

$$\varphi = k \cdot e^{-E/(RT)} \quad (2)$$

where E is the effective activation energy of the process. Semenov assumes that the condition for a sudden growth of velocity is the attainment of a certain critical velocity v_{control} when the probability of branching already approaches the probability of termination. This critical velocity is constant for a given process:

$$v = v_{\text{control}} = \text{const.} \quad (3)$$

The time which elapses to attain this critical velocity may be taken as the induction period τ . In agreement with Equation (1), it follows that $\varphi \cdot \tau =$

const., or according to Equation (2):

$$\tau = \frac{\text{const.}}{\varphi} = k' \cdot e^{E/(RT)} \quad (4)$$

The effective activation energy can, therefore, be determined from the temperature dependence of the length of the induction period. The values of the induction periods must of course be determined by an uninterrupted test. The difference between interrupted and uninterrupted tests becomes evident only at higher temperatures by lengthening of the induction period obtained in an interrupted test. As can be seen from Figure 10, the dependence of $\log \tau$ on the inverse value of the absolute temperature is linear. The oxidation of rubber is, therefore, controlled by Equation (4). From the angle of the curves it can be computed that the effective activation energy for the formation of carbonyl groups is 21,200 cal./mole and the effective activation energy for the formation of hydroxyl groups 21,300 cal./mole. Both energies are practically identical, which indicates a close relation between the mechanisms of formation of the two components. The measured value of the activation energy is smaller than the normal energy between molecules, and equals in order of magnitude the values given by Semenov for chain reactions. This verifies the radical character of the mechanism of oxidation of natural rubber.

The value found for the activation energy was checked by us also by another method, based on the validity of Arrhenius equation for the relationship between the velocity of oxidation and temperature. From the kinetic curves it is comparatively easy to determine the maximum velocity $v_{\max.}$ as the maximum tangent to the curves describing the dependence of extinction growth on time at different temperatures. If the dependence of $\log v_{\max.}$ on $1/T$ is plotted (Figure 11), a straight line is obtained, which verifies the validity of the equation:

$$v_{\max.} = k \cdot e^{-E/(RT)}$$

for the oxidation process of rubber. From the slope of this straight line the value of the effective activation energy for the formation of C=O groups may be computed, viz., $E = 21,000$ cal./mole, which coincides closely with the value obtained from the temperature dependence of the induction periods.

SUMMARY

Structural changes in natural rubber (expressed as changes in amounts of C=O, O—H, and C=C groups) caused by elevated temperature in the range of 60–160° C were followed quantitatively by means of infrared spectroscopy. In contrast to light aging, heat aging shows uniform progress throughout the whole thickness of the sample at temperatures above 90° C, below this temperature however, it is partially a surface reaction. The curves of relationships of the amounts of C=O and O—H groups and time have parallel courses with the difference that the amount of hydroxyl groups, after having reached a maximum, gradually drops. The heights of the kinetic curves (having a typical S-shape) are a function of temperature. They have their maxima in the range of 75–95° C, and above a certain temperature limit (C=O 120° C, O—H 100° C) they show no further changes. The activation energy computed from the lengths of the induction periods is practically the same for both groups (21,200 cal./mole for C=O, 21,300 cal./mole for O—H). This value checks

well with the activation energy computed from the dependence of maximum oxidation velocity on temperature (21,000 cal./mole).

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- ¹⁰ In the legend of the diagram, the extinction values of the control band A_{control} for the respective film are given in parentheses.
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VI. AGING BY HEAT AND LIGHT. DISCUSSION

ALEXANDER TKÁČ AND VOJTECH KELLÖ

Studies up to the present time of the heat and light aging of rubber by means of infrared spectroscopy¹ when compared with information in the literature, lead to certain conclusions regarding the mechanism of aging as well as the relationship between oxidation, structural changes, and mechanical properties.

EXPERIMENTAL PART

The equipment used, the preparation of samples, and the experimental technique have been described in previous papers². Since one of the main problems in the study of the aging of rubber is the absorption of oxygen, we have developed an informative method for determining the oxygen in carbonyl and hydroxyl groups. To determine the extinction coefficients in the respective functional groups of the macromolecular substances it was impossible to make use of data at present available (which are applicable only to ordinary organic compounds in the liquid phase), since the extinction coefficients are subject to appreciable changes with state, and also are influenced by the chemical nature of the substance as well as by the measuring equipment itself³. As a well defined macromolecular substance which is capable of forming films, we used cellulose acetate; and determined the extinction coefficients by a comparison of the amounts of C=O and O—H groups determined analytically and the extinctions of their absorption bands for a known thickness of the sample.

The cellulose acetate employed contained 52.1 per cent of acetyl groups, determined by the Eberstadt method⁴, which corresponds to 24.3 per cent of carbonyl groups bound by ester linkages. The number of O—H groups was computed from the difference of the total number of OH groups in cellulose and the number of acetyl groups in the given sample. Figure 1 shows the dependence of the extinction of C=O and O—H bands on the thickness of the sample. The thickness was determined by a contact measuring device as the mean value of a great number of measurements (with accuracy ± 0.003 mm.). The percentage extinction coefficient thus determined has a value of 82 for the ester carbonyl groups and 34 for OH groups [(g. %·cm.)⁻¹]. By using adequate amounts of substances, we found that in chloroform solution the value of the extinction coefficient of ester carbonyl groups (in ethyl acetate) was 191. For the aldehydic and ketonic C=O groups in solution (in formaldehyde and acetone, respectively) however, only about half of this value (80–88) was obtained. For acids in solution (acetic acid) we found the extinction coefficient to be 232. Assuming that this relation of the extinction coefficients is maintained in the solid phase, we obtain for the aldehydic and ketonic groups in solid films an approximate value of the percentage extinction coefficient of 36. Since the accuracy of spectroscopic measurements in the optimal case is ± 0.020 , it is possible in films of an average thickness of 0.005 cm. to determine reliably the changes of the amounts of carbonyl ester groups up to 0.05 per cent, of carbonyl aldehydic groups to 0.1 per cent, and of hydroxyl groups to 0.12 per cent. (In

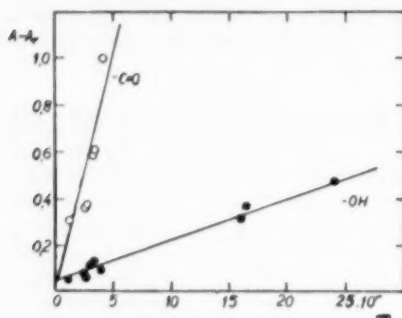


Fig. 1.—Dependence of extinction (corrected for light dispersion) of absorption band of carbonyl (ester) groups and hydroxyl groups in cellulose acetate on thickness of film.

case of O—H groups it is necessary to make a correction for moisture, which influences the measurement⁶.)

RESULTS AND DISCUSSION

ABSORPTION OF OXYGEN AND CHANGES IN PROPERTIES OF RUBBER

A fundamental problem in studying the aging of rubber is the absorption of oxygen and the determination of amounts of oxidized components. The total oxygen absorption, followed by direct methods, exhibits a linear growth with time⁶. In general, it has been found that a substantial degradation of rubber and corresponding changes in mechanical properties take place even with very low absorption of oxygen⁷. Thus Farmer and Sundralingam⁸ found that the molecular weight of rubber drops to one-third of its original value after absorption of 0.7 per cent of oxygen. A further absorption of oxygen shows only a slight effect on the molecular weight⁹ (see Figure 2). Blake¹⁰ observed that in light aging 1 per cent of absorbed oxygen is enough to cause an almost complete loss of tensile strength. Kemp, Ingmanson and Müller¹¹ found that, while a decrease of strength by one-half at 60° C is accompanied by 1.2 per cent ab-

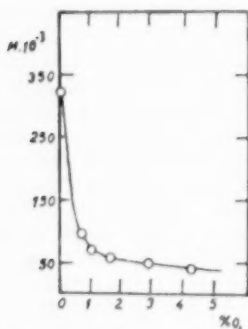


Fig. 2.—Decrease of molecular weight of rubber with oxygen absorption, according to Farmer and Sundralingam⁸.

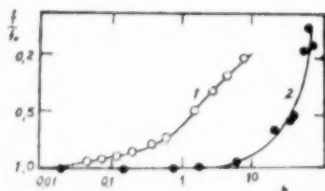


Fig. 3.—Comparison of change of relaxation (1) with increase of carbonyl groups, and (2) with time, in vulcanized rubber at 110° C, according to D'Or and Kössler¹².

sorption of oxygen, for an equal decrease of strength at 120° C an absorption of 0.65 per cent oxygen is sufficient. Without an access of oxygen however, heating does not cause any change of physical properties. D'Or and Kössler¹² compared their results of spectroscopic studies with changes of the mechanical properties of vulcanized rubber, and found that the loss of mechanical strength at 110° C takes place before the increase of C=O groups had become evident in the spectrum (Figure 3).

A comparison of the direct determination of oxygen absorption by GR-S rubber with the spectroscopic results of Field, Woodford, and Gehman¹³ shows that the minimum amount detectable by infrared spectroscopy is 0.5 per cent

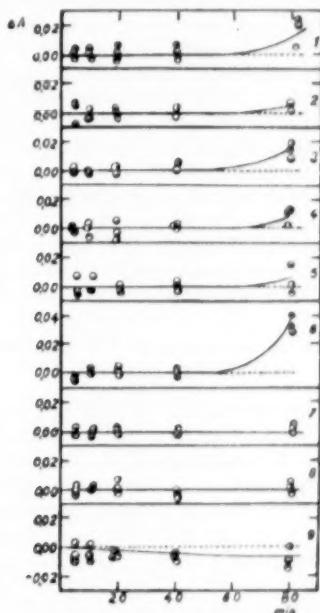


FIG. 4.—Changes in extinction of absorption bands of extracted natural rubber with time at 120° C—4 parallel series, film thickness 0.005 cm.; measurements taken after 4, 19, 42, and 82 min. 1. $-\text{CH}_2-\text{CH}_2-$ (11.95 μ), 2. $-\text{CH}=\text{CH}_2$ (11.25 μ), 3. $-\text{C}-\text{C}-$ (10 μ), 4. $-\text{C}-\text{O}-\text{C}-$ (9 μ), 5. CH_2 $-\text{C}=\text{C}-$ (6 μ), 6. $-\text{C}=\text{O}$ (5.8 μ), 7. Dispersion (5.24 μ), 8. Associated $-\text{OH}$ (2.96 μ), 9. Free $-\text{OH}$ (2.86 μ).

for the O—H groups, and 0.1 per cent for C=O (ester) groups. In spite of the fact that up to 5 per cent of absorbed oxygen was determined volumetrically, there was only one change observable in the spectrum, in the region of 10 μ . The parallel increase of extinction with absorption of oxygen in this region of the spectrum is ascribed by Field, Woodford, and Gehman to a growth of ether bonds.

However, in the heat aging of natural rubber, even after very careful measurements of thick films (0.005 cm.), and with a high-sensitivity spectrometer, we did not notice any change in the spectral zone 2.7–11.5 μ in the induction period of the kinetic curves of increase of oxidized groups. In this connection we studied quantitatively (see Figure 4) the amounts of isoprene groups

(11.95 μ), the region of 10 μ , C—O—C groups (9 μ), C=C groups (6.0 μ), C=O groups (5.82 μ), and free hydroxyl groups (2.86 μ) and associated hydroxyl groups (2.96 μ). Although there were no noticeable changes in chemical structure during the induction period, which, in case of a carefully extracted rubber would last approximately 100 minutes at 120° C, the differences in physical properties were evident after 50 minutes, e.g., in about one-half of the induction period.

Assuming, in accordance with several authors cited above, that the process of oxygen absorption bears a linear relationship with time, we attempted to compare the amount of spectroscopically determinable bound oxygen with the volumetric figures obtained by the method described in the experimental part. If we consider that in a period of time when the change of physical properties becomes evident, the increase of extinction is at the most only 0.010 (taking into account that in a fully oxidized rubber there is approximately 40 per cent oxygen bound by ether bonds¹⁴), the corresponding calculation, in the best case, gives a maximum value of 0.15 per cent. This is clearly below the value obtained by volumetric methods which has a minimum of 0.5^{11,14,21-23} per cent¹⁴.

So the question remains open in what form the oxygen is present in this physically considerably altered rubber, since it is combined by direct chemical bonds to only a limited degree. An aid in explaining this problem are the experimental results of our studies of the effects of heat and light¹⁶, which point to a variable number of active centers susceptible to oxidation at different conditions of temperature, intensity of irradiation, and catalysts.

INFLUENCE OF REACTION CONDITIONS ON THE DEGREE OF OXIDATION

It is generally agreed that sensitivity to oxidation is related directly or indirectly to the number of double bonds⁷. Kuzminskii and Lezhnev¹⁷ found a linear relationship between the number of double bonds and the velocity of oxygen absorption for various rubbers. Up to now, however, little attention has been paid to the degree of oxidation, which bears a relationship on the one hand to the total amount of centers sensitive to oxidation, and on the other hand to a mutual interdependence of the velocity of oxidation and spatial chain-linking¹⁸.

The height of the stationary sections of our kinetic curves, expressing the termination of a certain stage of rubber oxidation, depends on reaction conditions. This indicates that the total number of centers formed is not constant but varies with the temperature and the presence of catalysts. If we assume a relationship of active centers only to the total number of double bonds, their number would have to be dependent on the reaction conditions. However, as was shown by our quantitative measurements as well as by analytical determinations¹⁹, the number of double bonds remains practically unchanged during oxidation and also during vulcanization and is not influenced noticeably even by changes in the reaction conditions. Even at a constant temperature we can change substantially the height of the stationary sections of the curves by the addition of a catalyst, such as copper (mainly in the form of monovalent ions, see Figure 5). By increasing the temperature it is possible to cause further oxidation up to the stationary section of the respective higher temperature in a sample which has already attained the stationary section at the original lower temperature. The most remarkable change, however, takes place even at low temperatures by the action of ozone (Figure 6), in which case the oxidation is so

effective that in films of ordinary thickness the stationary zone is not even attained. As may be seen from Figure 6, oxidation by ozone shows on the whole a different characteristic. This subject will be dealt with later.

The facts disclosed above indicate that the essential properties of natural rubber must be sought in its inherent colloid structure.

The question of the structure of rubber has not yet been solved. Thus Houwink⁷ assumes a three-dimensional net structure of rubber aggregates, as does Meyer²⁰ and in some respects also Staudinger²¹. Kuhn's viscometric measurements²² lead to a visualization of coils formed out of rubber aggregates. James and Guth²³ assume a diamondlike structure, the structural rubber elements differing from a normal solid by special very easily deformable bonds. A new

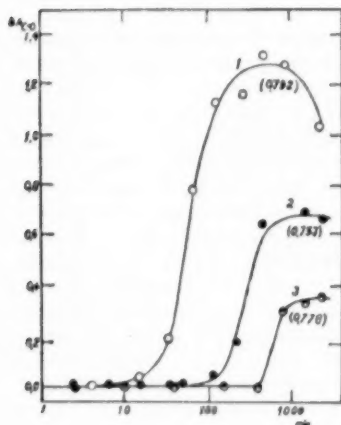


FIG. 5.—Kinetic curves of oxidation of extracted natural rubber at 130° C. 1. With 0.1% CuCl content. 2. Without any admixture. 3. Containing zinc oxide, tetramethylthiuram disulfide, mercaptobenzothiazole, stearic acid, and a mixture of benzidine and pyrogallol 1:1. In parentheses are the thicknesses of the films expressed by extinction of control band.

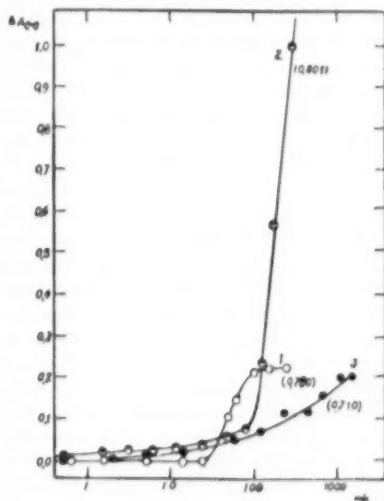


FIG. 6.—Changes of extinction of carbonyl groups in natural rubber (extracted pale crepe) with time. Irradiation by mercury lamp L-3 at 11 cm. through quartz mantle of gas cuvette: 1. In air, 2. In ozone of concentration approximately 2.7 mg.O₃ per liter of air. 3. Effect of ozone in given concentration in darkness at 23° C.

unusual concept of rubber structure is that of Feuchter²⁴, who prepared a natural rubber with unimpaired inherent structure ("total rubber"). After having studied its properties, he assumed a so-called polar rubber structure according to which the basic element is a complex of eight isoprene molecules, which can be considered to be an eight-valent radical, capable of forming spatial compounds and thus forming a rubber aggregate.

Many of our observations seem to support a concept of a rubber structure which is easily degraded spatially and again rebuilt, e.g., aggregated and disaggregated. Disaggregation leads to the formation of active centers (free radicals). In this way it is possible to explain, first of all, the difference of degree of oxidation at different temperatures. It may be assumed that, in the temperature range of 80–110° C, e.g., above the transition temperature of elastic to plastic modification of rubber, there is a very efficient disaggregation which

leads to a rapid increase of active centers. Corresponding to this process, the heights of the stationary zones of the kinetic curves show an ascending trend. A further growth of the number of active centers, which after reaching 120° C, shows only a very slight upward tendency, can be attained by active catalysts (Figure 5) or by the action of ozone (Figure 6). In the presence of substances which retard the oxidation of free radicals, and thereby establish favorable conditions for retrogressive aggregation (antioxidants, vulcanizing agents), the stationary sections of kinetic curves will be the lower (Figure 5) the higher the degree of lateral chain formation (linkage) e.g., retrogressive aggregation (vulcanization). Since all changes of physical properties such as mechanical strength, tackiness, and viscosity take place for the most part during the induction period, when changes in chemical structure are not yet apparent, it is reasonable to assume that the rheological properties depend principally on the colloidal structure of rubber, and that the presence of oxidized groups is a factor of secondary importance. Oxygen, which is absorbed by rubber earlier than its presence in a chemically bound form can be detected, is probably adsorbed on the active centers, thus preventing on the one hand retrogressive aggregation, and, on the other hand becoming activated (chemosorption) and after a certain period introducing the chain process of oxidation. On this basis, a number of phenomena can be explained, e.g., tackiness in the induction period, an increase of sensitivity to oxidation during milling²⁴, to a certain degree the surface character of aging, the effect of extraction on physical properties, and the fact that neither oxidation nor vulcanization brings about any substantial change of the number of double bonds. This is also to be associated with a low quantum yield (of the order 10^{-4}) by photocatalysis²⁵. However, the existence of an absorption band at 6μ , belonging to olefinic double bonds, is at variance with the concept of an internally saturated structure of rubber without double bonds. It is necessary to consider, however, that rubber obtained by the conventional process from natural latex is no longer in a natural form, but is degraded to a considerable degree, and this may explain the presence of olefinic double bonds. To decide how far the absorption band at 6μ warrants the assumption of the unsaturated nature of the rubber would require a direct spectroscopic study of rubber in its original state. The results of some authors²⁷ may be informative, according to which the extinction coefficient of the band pertaining to C—C groups increases with stretching, while at the same time the extinction of the band in the region of 6μ decreases. Since elastic changes are related to changes in colloidal structure, the absorption spectral bands, which change with the deformation, necessarily must be closely related to the internal structure. In this connection attention should be called to the fact that our values for the activation energy of rubber²⁸ coincide closely with the value of 21–23 kcal./mole, which, by an entirely different method, and in the presence of antioxidants, was found by Kuzminskii and Lezhnev¹⁷, and which is ascribed by these authors to activation of double bonds. However, it could not be excluded that the measured activation energy is related to the formation of radicals by the destruction of the original structure.

MATHEMATICAL FORMULATION OF THE SHAPE OF REACTION CURVES

The time course of oxidation catalyzed by light and heat can in both cases be expressed by similar kinetic dependences which, in a graphic representation of extinction growth with time (proportional to the amount of oxidized groups), show a characteristic S-shape. The dependence of the increase of oxidized

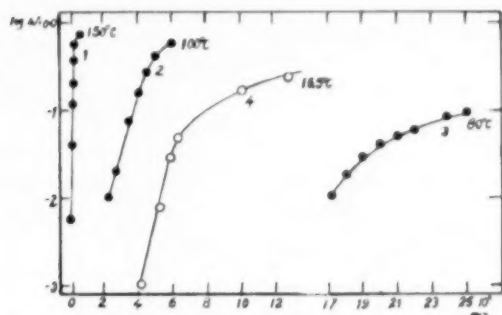


Fig. 7.—Dependence of $\log \Delta A c_{\infty}$ on time t for the heat and light aging of extracted natural rubber (verification of the extent of validity of the relation: $A = k e^{\varphi t}$). 1. 150° C, 2. 100° C, 3. 80° C, 4. Irradiated by mercury lamp L-4 at 15 cm. and 16.5° C.

groups on time is expressed in its initial stages, with sufficient accuracy, by the Semenov equation for branched chain-reactions:

$$\Delta A = C \cdot e^{\varphi t} \quad (1)$$

where C and φ are constants, ΔA is the increase of extinction proportional to the number of oxidized groups in time t . For the first moments the relation: $\Delta A = k \cdot t + C \cdot e^{\varphi t}$ applies more accurately. The experimental curves conform the better with the Equation (1), (which for aging was first applied by D'Or and Kössler¹²), the higher is the temperature of oxidation. At lower temperatures, i.e., at 80° C (Figure 7), as well as in the case of photocatalytic oxidation, we can observe on the curves of $\log \Delta A$ as a function of time t marked deviations from linearity, which indicate a limited applicability of Equation (1) for the oxidation of rubber. These deviations are probably related to the surface char-

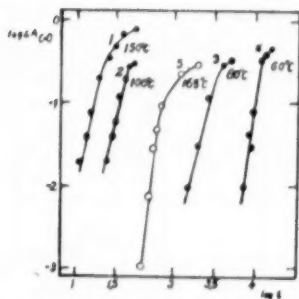


Fig. 8.—Dependence of $\log \Delta A c_{\infty}$ on $\log t$ for heat and light aging of extracted natural rubber (verification of the extent of validity of the relation: $\Delta A = k' \cdot t^a$). 1. 150° C, 2. 100° C, 3. 80° C, 4. 60° C, 5. Irradiated by mercury lamp L-4 at 15 cm. and 16.5° C.

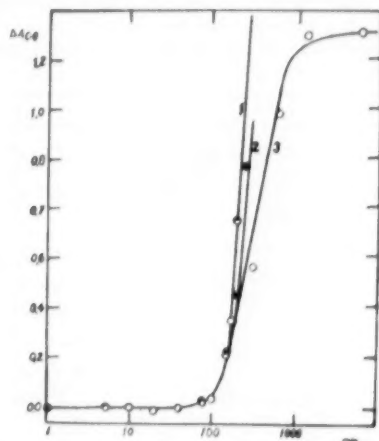


Fig. 9.—Comparison of courses of kinetic curves. Curves computed according to the relation: 1. $\Delta A = k \cdot e^{\varphi t}$; 2. $\Delta A = k' \cdot t^a$; 3. Experimentally determined curve. Uninterrupted aging at 120° C. Average film thickness expressed by extinction of control band (0.720).

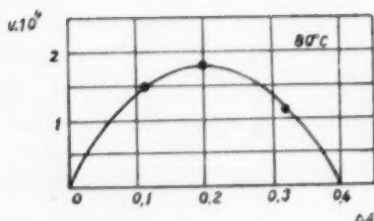


FIG. 10.—Dependence of velocity of oxidation of extracted natural rubber on the number of oxidized groups at 80° C. Curve constructed according to Equation (4). Circles denote experimental points.

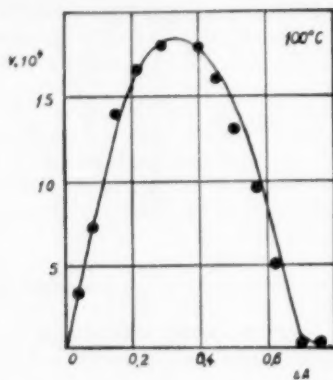


FIG. 11.—Dependence of velocity of oxidation of extracted natural rubber on the number of oxidized groups at 100° C. Curve constructed according to Equation (4). Circles denote experimental points.

acter of light aging²⁶ and heat aging²⁸ below 80° C or to conditions favorable to spatial crosslinking (vulcanization)²⁹. In all the cases considered, the empirical relation (Figure 8) gives a better representation:

$$\Delta A = k' \cdot t^a \quad (2)$$

Figure 9 shows a comparison of the experimental curve (at 120° C) with the curves computed from relations (1) and (2).

The curves of the dependence of the velocity of oxidation ($v = d(\Delta A)/dt$) on the number of oxidized groups (expressed by extinction of C=O groups, as in Figures 10–15) have a shape characteristic of autocatalytic reactions: after passing a maximum the velocity drops to zero. It is impossible however, especially at higher temperatures, to interpret these curves by a simple auto-

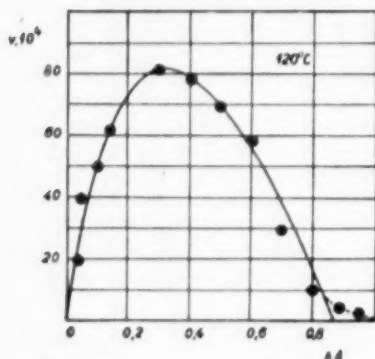


FIG. 12.—Dependence of velocity of oxidation of extracted natural rubber on the number of oxidized groups at 120° C. Curve constructed according to Equation (4). Circles denote experimental points.

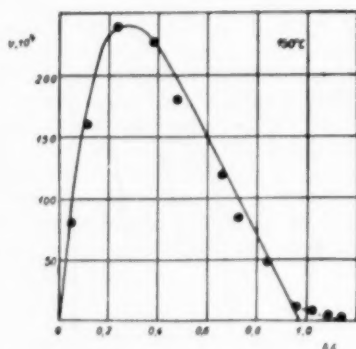


FIG. 13.—Dependence of velocity of oxidation of extracted natural rubber on the number of oxidized groups at 150° C. Curve constructed according to Equation (4). Circles denote experimental points.

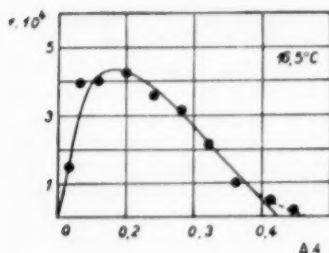


Fig. 14.—Dependence of velocity of oxidation of extracted natural rubber on the number of oxidized groups with irradiation by mercury lamp L-4 at 15 cm. and at 16.5° C. Curve constructed according to Equation (4). Circles denote experimental points.

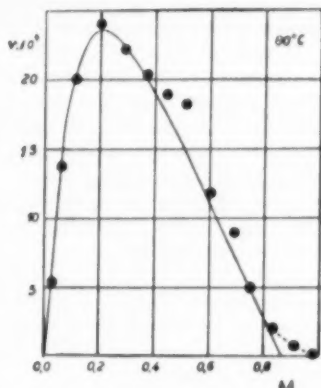


Fig. 15.—Dependence of velocity of oxidation of extracted natural rubber on the number of oxidized groups with irradiation by mercury lamp L-4 at 15 cm. and at 80° C. Curve constructed according to Equation (4). Circles denote experimental points.

catalytic equation:

$$w = k \cdot \eta (1 - \eta) \quad (3)$$

where $\eta = \Delta A / \Delta A_{\infty}$, and $w = d\eta/dt$, because the maxima of our experimental curves are not in the middle, for with temperature (and intensity of illumination) the maximum is shifted to the left. Our experimental results are very well described by the equation:

$$w = \frac{k}{b} (1 - e^{-b\eta}) (1 - \eta), \quad (4)$$

derived by Semenov³⁰ for a spatial case of branched reactions, the so-called negative mutual interaction of reaction chains, e.g., branched reactions where the velocity of termination is proportional to the second power of the concentration of free radicals (which we have already assumed for rubber¹⁸). In Equation (4), k is a velocity constant of the chain-branching reaction and b is a constant proportional to the termination velocity. Equation (3) is a special case of Equation (4) when $b \rightarrow 0$. With increase of the value b , the maximum of the curves is shifted to the left.

TABLE I
VALUES CHARACTERIZING THE VELOCITY CURVES AS A FUNCTION
OF THE NUMBER OF OXIDIZED GROUPS

	Temperature		v_{max}	w_{max}	k	$\log k$	b	Position of maximum	ΔA_{∞}	Figure
	(° C)	(° K)								
Heat aging	80°	353°	0.00018	0.00045	0.0018	0.255-3	0.1-0.2	-0.50	0.400	10
	100°	373°	0.00185	0.00265	0.0119	0.076-2	0.5	0.47	0.700	11
	120°	393°	0.0082	0.0093	0.065	0.813-2	2.9	0.36	0.880	12
	150°	423°	0.024	0.025	0.256	0.408-1	6.0	0.28	0.960	13
Light aging	16.5°	—	0.00043	0.00132	0.015	—	7.0	0.26	0.324	14
	80°	—	0.0024	0.0028	0.34	—	8.2	0.24	0.860	15

Table I gives experimental values characterizing the curves of velocity as a function of the number of oxidized groups under different conditions.

Figures 10-15 show clearly a side process proceeding at low velocity after the curves of relationship between extinction and time have reached the stationary region, causing a deviation of experimental points from the course given by Equation (4). It seems that these subsequent accompanying reactions are induced by transformation of intermediary products (mainly aldehydes) to higher oxidized forms. These reactions can be accelerated noticeably, for example by catalysts (copper), which is markedly expressed by a rapid drop of the extinction vs. time curves after they have reached their maximum (Figure 5).

If we plot in Arrhenius coordinates the dependence of the velocity constant k on the temperature, a straight line is obtained (see Figure 16), and its slope enables us to obtain for the activation energy the value 21-22 kcal./mole, which is in very close accord with our previous results²⁸ as well as with the findings of other authors¹⁷.

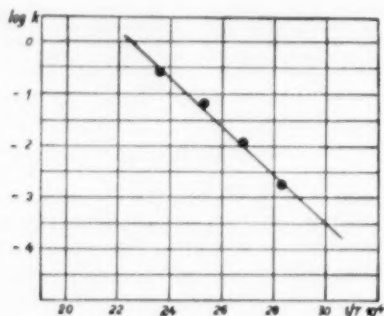


Fig. 16.—Dependence of the logarithm of the constant of oxidation velocity on the inverse value of the absolute temperature for the heat aging of natural rubber.

CONCLUSIONS

Evaluating the results of the study of the effects of light and heat on rubber by means of infrared spectroscopy, certain conclusions seem justified. Light aging as well as heat aging are governed by mathematical relations which apply to degenerate chain reactions with negative mutual interaction of chains, the difference between light and heat effect being evident by different values of the constants. Light aging shows a well defined surface character. The physical changes caused by light and heat do not take place in the same stages of oxidation. For instance, tackiness resulting from light aging appears only after a larger proportion of oxygen has been bound structurally (in the middle portions of the steep ascent of the kinetic curves), whereas in heat aging it occurs at the beginning of the ascending course. This also indicates that the physical properties of rubber are related primarily to the degree of disaggregation and retrogressive aggregation, and indirectly related to the amount of structurally combined oxygen. The secondary oxidizing reactions, as indicated by infrared spectroscopy, are a good criterion for the evaluation of the interrelation between oxidative degradation and spatial crosslinking (vulcanization), as two alternatives of parallel processes caused by preceding disaggregation. It is, therefore, possible to make use of the method for the evaluation of the effects of

different compounding ingredients, such as initiators, catalysts, inhibitors, retarders, and vulcanizing agents⁶, not only in natural rubber but also in synthetic rubbers.

SUMMARY

Experimental results of spectroscopic studies of the heat and light aging of rubber indicate that the greatest degradation takes place during the induction period of oxidation. The energy consumed leads to deterioration of the internal structure of the macromolecules of rubber, and this causes changes in rheological properties. At the locations of degradation free radicals are formed, and these cause further oxidation. Different heights of the curves of the number of C=O and O—H groups as a function of time at different temperatures point to differences in the number of active centers susceptible to oxidation. Variable numbers of active centers are also proved by oxidation in the presence of ozone and of copper as catalyst, and in the milling process. These changes correspond to the transition of elastic rubber into its plastic form at approximately 80° C. The relationship between velocity of heat and light oxidation w and concentration of oxidized groups η is given by the equation: $w = k/b [(1 - e^{-b\eta})(1 - \eta)]$. This points to a chain mechanism of branched reactions, with mutual negative interaction of the chains. In light aging the initiation is more intensive and the surface character is more pronounced. Analysis of the experimental curves indicates that the heights of the kinetic curves are a measure of the formation of side chains in rubber during aging as well as during vulcanization.

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OXIDATIVE DEGRADATION OF SWOLLEN VULCANIZATES *

T. G. DEGTEVA AND A. S. KUZMINSKIĬ

SCIENTIFIC RESEARCH INSTITUTE OF THE RUBBER INDUSTRY, MOSCOW, U.S.S.R.

Oxidative degradation in swollen vulcanizates is closely related to the problem of rubber reclaiming. In reclaiming rubber by the solvent method, the breakdown of the vulcanizate structure is the result mainly by oxidation reactions which occur at the locations of the double bonds in the molecular chain of the rubber. We showed earlier¹ that when a vulcanizate is oxidized in the swollen condition there is a joint oxidation of rubber and solvent, which in large degree changes the character of the structural transformations.

The present investigation was undertaken by us with the aim of clarifying the basic principles underlying the oxidative degradation of swollen vulcanizates with different structures.

EXPERIMENTAL PART

All the vulcanizates studied were prepared on a base of industrial sodium-butadiene rubber (SK-B). The composition and properties of the vulcanizates are presented in Tables 1 and 2. The ratio between the weights of vulcanizate and solvent in the swollen vulcanizate amounted to 1:6.6. The solvent used was decalin.

OXIDATIVE DEGRADATION OF A SWOLLEN THIURAM VULCANIZATE

Figure 1 presents the results of an experimental study of oxidative degradation in a stock vulcanized with tetramethylthiuram disulfide (Thiuram)—the first type of stock. The figure shows that although there was no sign of oxygen absorption (Curve 4) nor of phenyl-2-naphthylamine consumption (Curve 1) for a period of 19 hours, there was at the same time a fairly rapid decrease of the equilibrium modulus (Curve 3) and a slight increase of the solubility (Curve 2). Only after this length of time did the autocatalytic oxidation reaction develop, accompanied by an intense oxygen absorption, a high rate of phenyl-2-naphthylamine consumption, and a rapid accumulation of soluble degradation products.

An analysis of the data presented indicates that phenyl-2-naphthylamine does not inhibit the oxidation process in its earlier stages. The action of phenyl-2-naphthylamine is revealed only in the autocatalysis in which the vulcanizate loses its elastic properties, and where in actual practice we are dealing with the products of widespread scission and structure formation in the vulcanizate. In the present case, the inhibition of the oxidative process is evidently brought about by the decomposition products of Thiuram.

In order to verify this hypothesis, the following experiments were carried out. A stock vulcanized with Thiuram was extracted with acetone for 50 hours.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from the *Zhurnal Prikladnoi Khimii*, Vol. 28, No. 12, pages 1314-1321 (1954).

Then the extract was added to a thermal vulcanizate² which contained no phenyl-2-naphthylamine. Figure 2 presents curves for the oxidation of a swollen vulcanizate into which Thiuram decomposition products have been introduced. Here too, as one would expect, a measurable absorption of oxygen commences only after a prolonged induction period.

TABLE 1
RECIPES OF THE VULCANIZATES*

Composition of stock (parts by weight) and vulcanizing conditions	Type of vulcanizate			
	1	2	3	4
SK-B	100	100	100	100
Sulfur	—	2	6	—
Tetramethylthiuram disulfide	3	—	—	—
Zinc ethylphenyldithiocarbamate (II Extra N)	—	1	—	—
Diphenylguanidine	—	—	1	—
Zinc oxide	5	5	5	—
Stearic acid	2	2.5	2	—
Time of vulcanization (minutes)	90	20	20	200
Vulcanization temperature (° C)	143°	90°	143°	220°

* The figures show the parts by weight of the compounding ingredients per 100 parts by weight of rubber.

Data in the literature³ on the thermal decomposition of tetramethylthiuram disulfide in the presence of zinc oxide indicate the existence of a whole series of decomposition products, including carbon disulfide, sulfur, hydrogen sulfide, dimethylamine, tetramethylthiourea, and zinc dimethyldithiocarbamate.

Among the above-mentioned substances, sulfur is well known for its inhibiting action. Further, it has been shown that zinc diethyldithiocarbamate is not an effective inhibitor. However, we cannot be sure that among all the thiuram decomposition products, sulfur alone plays the part of a regulator of the oxidative process. This question requires further investigation.

TABLE 2
CHARACTERISTICS OF THE VULCANIZATES*

Type of vulcanizate	Analysis (per cent by weight)				Solubility in benzene (per cent)	Maximum swelling in benzene (per cent)	Equilibrium modulus (kg./sq. cm.)
	Phenyl-2-naphthylamine	Total sulfur	Combined sulfur	Free sulfur			
1	0.31	0.99	0.49	—	11	550	8.6
2	0.43	—	0.74	—	—	350	11.4
2a**	0.55	—	—	—	0.14	—	18.4
3	0.39	4.8	2.56	2.24	8	480	9.8
4	0.6	—	—	—	14.9	460	8

* In this table, the values are recorded as percentages by weight of the rubber.

** Vulcanizate 2a was cured 80 minutes instead of 90 minutes.

OXIDATIVE DEGRADATION OF A SWOLLEN ZINC ETHYLPHENYLDITHIOCARBAMATE VULCANIZATE

The rubber was vulcanized with zinc ethylphenyldithiocarbamate at 90° C for 80 minutes, thereby excluding the possibility of carbon crosslinks being formed by means of thermal structure formation in this type of vulcanizate. The structural network of this type of vulcanizate was built entirely with sulfur bonds.

Figures 3 and 4 show the kinetic curves for the oxidation of the swollen vulcanizate in the presence of antioxidants (free sulfur and phenyl-2-naphthylamine) as well as in their absence. The action of sulfur and phenyl-2-naphthyl-

amine in the oxidation of a swollen stock causes an induction period (about 2.5 hours). Subsequent oxidation proceeds at a constant rate. In the induction period the oxidative process is controlled only by the free sulfur; this, in being consumed, inhibits the action of the phenyl-2-naphthylamine (Figure 5). The accumulation of soluble products proceeds at a more rapid rate during the induction period than it does in the latter stages of the process. When a vulcanizate containing sulfur and phenyl-2-naphthylamine is oxidized, no stable peroxides are found among the oxidation products.

The viscosity of the sol fraction of the oxidized vulcanizate containing an antioxidant varies directly with the concentration of the solution (Figure 6). These data indicate that the oxidative degradation proceeds at a constant rate.

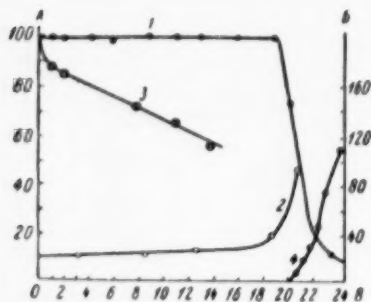


FIG. 1.—Effect of phenyl-2-naphthylamine and Thiuram decomposition products on the kinetics of oxidation of a vulcanizate swollen in decalin at 155° C. 1. Consumption of phenyl-2-naphthylamine. 2. Change of solubility. 3. Change of the conditional equilibrium modulus of elasticity. 4. Kinetics of the oxidation of a stock vulcanized with Thiuram. The abscissa represents the time in hours. Ordinate A represents the consumption of phenyl-2-naphthylamine, the solubility and the equilibrium modulus (all in per cent); ordinate B the amount of oxygen absorbed, in millimoles/mole.

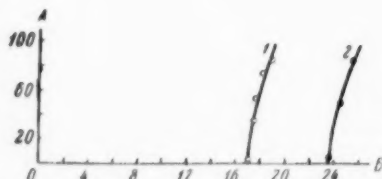


FIG. 2.—Effect of phenyl-2-naphthylamine and Thiuram decomposition products on the kinetics of the oxidation of an extracted thermal vulcanizate in a medium of decalin at 155° C. Curves 1 and 2 represent separate experiments. The abscissa represents the time in hours; the ordinate the amount of oxygen absorbed, in millimoles/mole.

OXIDATIVE DEGRADATION OF A SWOLLEN DIPHENYLGUANIDINE VULCANIZATE

Figure 7 presents curves characterizing the oxidation of a stock vulcanized with diphenylguanidine. It is known⁴ that polysulfide bonds predominate in the structure of a vulcanizate of this type. It is seen from the figure that the absorption of oxygen proceeds at a constant rate (Curve 1). In the course of the oxidation of a swollen vulcanizate, it is noted that phenyl-2-naphthylamine (Curve 2) and free sulfur (Curve 3) are both being consumed at the same time. The rate of consumption of phenyl-2-naphthylamine drops considerably after 7 hours of oxidation, while the solubility of the vulcanizate reaches its maximum value at the same point in time. Thus we see that only an efficient inhibiting action can affect the degradation of the vulcanizate. In the present case the free sulfur does not interfere with the consumption of phenyl-2-naphthylamine. It may be supposed that, because of the presence of an accelerator in the stock, a vulcanization process develops in conjunction with the oxidation. Experiments which we set up have confirmed this assumption. As Figure 7 demonstrates, when a vulcanizate without solvent is heated in the absence of oxygen,

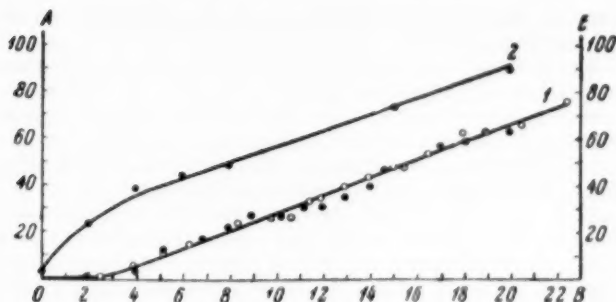


Fig. 3.—Kinetics of oxidation of the swollen vulcanizate 2a in the presence of phenyl-2-naphthylamine and free sulfur, and the change of its solubility during oxidation at 150° C. 1. Kinetics of oxidation. 2. Change of solubility. The abscissa represents the time of oxidation in hours; ordinate A the amount of oxygen absorbed, in millimoles/mole (Curve 1), and ordinate B the solubility in per cent (Curve 2).

the consumption of sulfur is even more rapid, so that after five hours' heating only 0.15 per cent free sulfur remains in the stock.

OXIDATIVE DEGRADATION OF A SWOLLEN THERMAL VULCANIZATE

The formation of the structure of thermal vulcanizates² is based on the creation of carbon crosslinks. We chose the thermal vulcanizate as a network

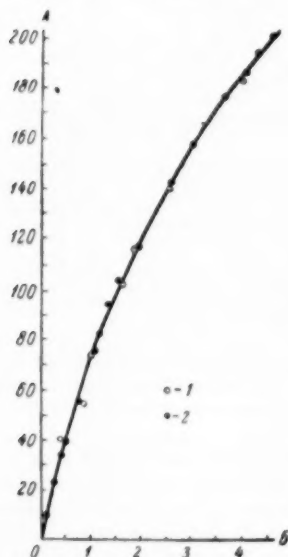


Fig. 4.—Kinetics of oxidation of swollen vulcanizates at 150° C. 1. Thermal vulcanizate in decalin. 2. Vulcanizate with zinc ethylphenyldithiocarbamate in decalin. The abscissa represents the time of oxidation in hours; the ordinate the amount of oxygen absorbed, in millimoles/mole.

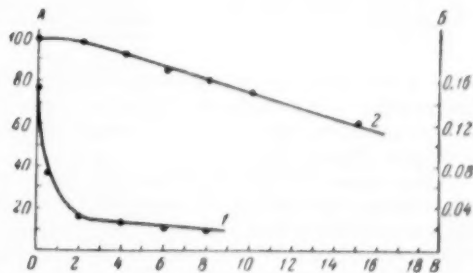


Fig. 5.—Consumption of phenyl-2-naphthylamine and free sulfur during the oxidation of vulcanizate 2a at 150° C. 1. Free sulfur. 2. Phenyl-2-naphthylamine. The abscissa represents the time in hours; ordinate A represents the phenyl-2-naphthylamine content, in per cent of the initial content, and ordinate B the free sulfur content in per cent.

type without any sulfur, since sulfur has a considerable effect on the nature and rate of oxidative processes.

Figure 8 presents the kinetic curves for oxidation of a swollen thermal vulcanizate at 150° C. The presence of phenyl-2-naphthylamine in the system brings about an induction period. It is observed that during the oxidation of a swollen thermal vulcanizate containing phenyl-2-naphthylamine the antioxidant is being consumed, and that the decalin has a considerable effect on the characteristics of the antioxidant consumption (Figure 9).

Although in unswollen rubber phenyl-2-naphthylamine is consumed at a linear rate during the induction period, in a vulcanizate which has been swollen about 65 per cent of the initial antioxidant content remains at the end of the induction period. The highest rate of phenyl-2-naphthylamine consumption is observed in the initial stage of autocatalytic oxidation, before the combined oxygen content has reached 20–25 millimoles/mole of rubber.

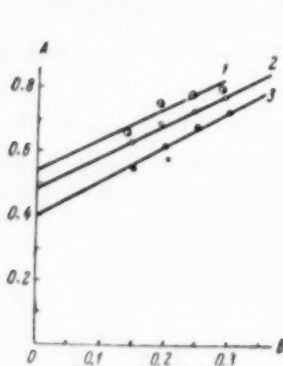


Fig. 6.—Change of the reduced viscosity of the sol fraction of stock 2a (containing antioxidant) when oxidized in a swollen condition. 1. Oxidized for 6 hours. 2. 15 hours. 3. 20 hours.

The abscissa represents the concentration c of the solution, in g. per 100 ml.; the ordinate the reduced viscosity μ_{sp}/c .

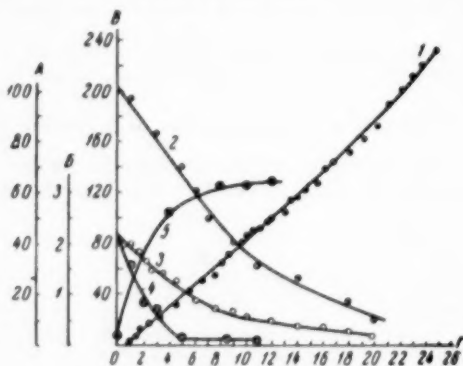


Fig. 7.—Effect of the antioxidants present in a vulcanizate of type 3 on the kinetics of its oxidation in a swollen condition at 150° C. 1. Kinetics of oxidation of the vulcanizate. 2. Phenyl-2-naphthylamine content. 3. Free sulfur content. 4. The same, in a vacuum without solvent. 5. Change of solubility. The abscissa represents the time of oxidation in hours. The left-hand ordinate represents the phenyl-2-naphthylamine content in per cent of the initial content, and the percent solubility; the middle ordinate the free sulfur content in per cent; the right-hand ordinate the amount of oxygen absorbed, in millimoles/mole.

It is important to note that the kinetic curve of phenyl-2-naphthylamine consumption in a swollen thermal vulcanizate is almost an exact duplicate of the corresponding curve for the consumption of this antioxidant in the oxidation of decalin (Figure 10).

The example cited clearly shows that the behavior of antioxidants in swollen vulcanizates does not at all correspond to their action in unswollen stocks. Having established that a joint oxidation of rubber and solvent takes place in a swollen stock, we may now consider the part played by the antioxidant in this process from a new viewpoint. For it follows from the conception of a joint oxidation that the behavior of the antioxidant in a swollen stock is governed not only by the composition of the vulcanizate but also by the nature and quality of the solvent.

The accumulation of stable peroxides in the process of oxidation of a swollen thermal vulcanizate was also studied (Figure 11). The kinetic curve for per-

oxide accumulation passes through a maximum corresponding to 30–45 millimoles of absorbed oxygen per mole of rubber. The change of structure in the swollen vulcanizates during the oxidation process was traced through the change in their solubility and relaxation constant, determined with the Kargin dynamometric balance.

Figures 12 and 13 represent the kinetic curves for the change of solubility and relaxation constant. As the curves show, in the induction period there is an increase of the solubility and relaxation rate of a swollen vulcanizate when it

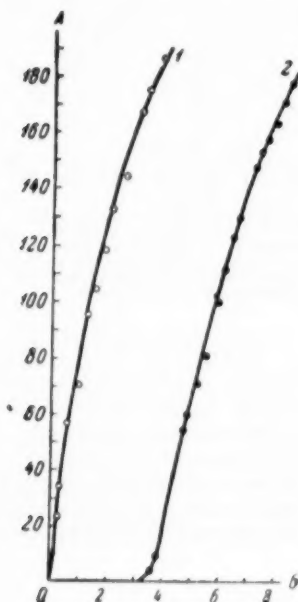


Fig. 8.—Effect of phenyl-2-naphthylamine on the kinetics of oxidation of a thermal vulcanizate swollen in decalin at 150° C. 1. Thermal vulcanizate in decalin. 2. The same in decalin with phenyl-2-naphthylamine. The abscissa represents the time in hours; the ordinate the amount of oxygen absorbed in millimoles/mole.

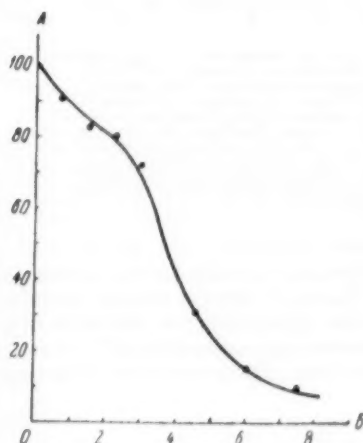


Fig. 9.—Consumption of phenyl-2-naphthylamine during the oxidation of a swollen thermal vulcanizate at 150° C. The abscissa represents the time in hours; the ordinate the phenyl-2-naphthylamine content, in per cent of the initial content.

undergoes oxidation. The increase in the solubility and relaxation rate of the stock attests to the prevalence of oxidative scission in the induction period.

It is evident from a comparison of Figures 11 and 12 that the intensive structure formation in a swollen thermal vulcanizate is brought about through a rapid decomposition of the stable peroxides.

On the basis of the results presented one may say that the decisive influence affecting the relative rates of the simultaneously occurring destruction and structure-forming processes, in the oxidation of swollen stocks, is that exerted by the antioxidants (phenyl-2-naphthylamine, free sulfur, and the accelerators and their decomposition products). Regardless of the original composition of the vulcanizate, the destructive tendency prevails only under a condition of in-

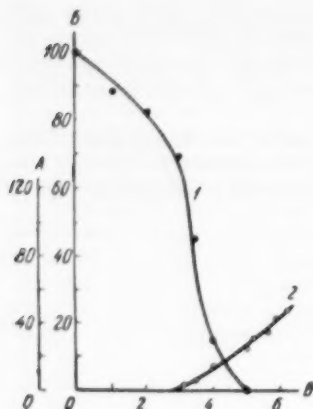


FIG. 10.—Antioxidant consumption in the oxidation of decalin at 150°C . 1. Consumption of phenyl-2-naphthylamine. 2. Kinetics of oxidation of decalin in the presence of phenyl-2-naphthylamine. The abscissa represents the time in hours; ordinate A represents the amount of oxygen absorbed in millimoles/mole, and ordinate B the phenyl-2-naphthylamine content in per cent of the initial content.

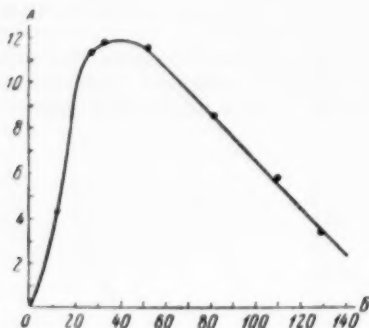


FIG. 11.—Kinetics of the accumulation of peroxides during the oxidation of a swollen thermal vulcanizate. The abscissa represents the amount of combined oxygen, in millimoles/mole; the ordinate the amount of oxygen present in the form of peroxides, in millimoles/mole.

hibited oxidation. The depletion of the antioxidant, in the oxidation of a swollen stock, brings about a process of structure formation in the stock.

Figure 14 shows a comparison of curves of the change of the solubility of swollen vulcanizates, as related to their combined oxygen content. The vulcanizates were extracted with acetone and methanol before being subjected to oxidation. The curves show that regardless of the type of structural network,

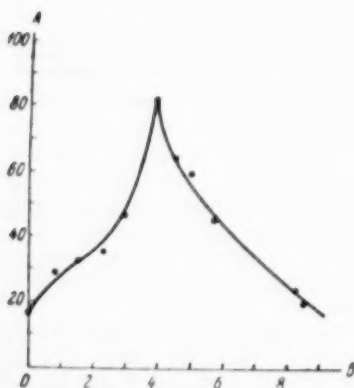


FIG. 12.—Change of solubility during the oxidation of a swollen thermal vulcanizate at 150°C . The abscissa represents the time in hours; the ordinate the per cent solubility of the stock.

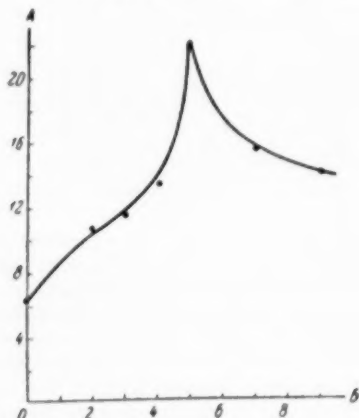


FIG. 13.—Change of the relaxation constant as related to the time of oxidation, in a swollen thermal vulcanizate. The abscissa represents the time of oxidation in hours; the ordinate the relaxation constant value $\times 10^{-4}$.

the accumulation of soluble products takes place only in the earlier stages of the oxidation of a swollen stock. At the stage where the destructive process prevails, a considerable quantity of soluble products appears; these enter into the structure-forming reaction, and, along with the insoluble portion of the stock, form the overall vulcanizate network. The development of a spatial structure causes a reduction of the degree of swelling, which leads to a partial separation of solvent from the swollen stock ("shrinkage"). A reduction in swelling, in turn, considerably accelerates the structure-forming process which was already in progress.

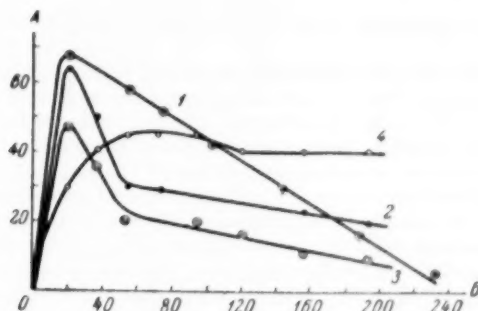


Fig. 14.—Change of solubility in the course of oxidation of extracted vulcanizates in a swollen condition at 150° C. 1. Thermal vulcanizate. 2. Stock vulcanized with zinc ethylphenyldithiocarbamate and sulfur (type 2). 3. Stock vulcanized with tetramethylthiuram disulfide. 4. Stock vulcanized with diphenylguanidine and sulfur. The abscissa represents the amount of oxygen absorbed in ml. on 0.2 g. of rubber; the ordinate the solubility in per cent.

It will be noted that there is a considerable difference in the behavior of antioxidants in swollen and in unswollen stocks. Such a variation in the action of antioxidants in these systems may be explained by the fact that, in the process of joint oxidation of solvent and rubber in a swollen vulcanizate, the free radicals formed have a different reactivity from those formed with rubber alone.

CONCLUSIONS

1. In the course of a study of the oxidative degradation of vulcanizates with different structures (a thermal vulcanizate, a vulcanizate with Thiuram, one with diphenylguanidine and, one with zinc ethylphenyldithiocarbamate) it was established that the swollen vulcanizate, regardless of the accelerator present, undergoes two simultaneous reactions—destruction and structure formation.

2. It was revealed that the dominance of the destructive process, in the oxidation of swollen vulcanizates, can occur only in the presence of antioxidants; and that only after a considerable consumption of antioxidant does the rate of structure formation equal or exceed the rate of destruction.

3. It was shown that the behavior of antioxidants in swollen vulcanizates is governed not only by the nature of the rubber, but also in large degree by the nature of the solvent.

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CHAIN SCISSION IN THE OXIDATION OF HEVEA. III. EFFECT OF TEMPERATURE *

E. M. BEVILACQUA

GENERAL LABORATORIES, UNITED STATES RUBBER CO., PASSAIC, NEW JERSEY

When molecular oxygen reacts with raw Hevea rubber in latex at 90° C, two molecules of carbon dioxide and two molecules of "volatile acid" (one molecule of acetic acid and one molecule of formic acid) are produced for each apparent scission of the hydrocarbon chain, estimated from changes of solution viscosity. This corresponds to the complete destruction of one isoprene unit, and if the several hydrocarbon end groups are oxidized, requires a minimum of six molecules of oxygen per scission¹. Estimates of oxygen requirements for scission during the accelerated oxidation of vulcanized Hevea rubber much lower than this have been made². It has been suggested that the apparent high efficiency of scission in vulcanized rubber is the result of the predominance of scission at crosslinks over random cutting of the hydrocarbon chain³. To investigate the less likely possibility that the mechanism of the reactions which leads to scission changes sharply with the rate of oxidation, the earlier estimates¹ of yields of scissions and of volatile acids during the oxidation of Hevea latex at 90° C have been supplemented by measurements at 70° C and at 110° C.

Some results of determinations of scission efficiency and of yields of volatile acids are summarized in Table I.

TABLE I
YIELDS OF ACIDS AND OF SCISSIONS

Temperature (° C)	70	90	110
Oxidation rate (mmoles/100 g.-hr.)	0.7	2.0	6.0
Per mole of oxygen:			
Scissions (mole)	0.037	0.054	0.062
Volatile acids (eq.)	0.071	0.095	0.118
Eq. acids/mole scissions	1.9	1.8	1.9

Carbon dioxide was not determined in these experiments, but was shown to vary directly with volatile acid by titration of the latexes after oxidation.

The results given in Table I show that in latex, there is no important change in the mechanism of scission within the temperature range of this investigation. Although the efficiency of the scission increases with the temperature, the ratio of acid produced to scissions remains constant.

EXPERIMENTAL

The latex used was similar to that used previously. Experimental procedures were as described before¹ except for oxidations at 110° C. These were

* Reprinted from the *Journal of Organic Chemistry*, Vol. 21, No. 3, pages 369-370, March 1956.

carried out in sealed twelve-ounce bottles fitted with nylon gaskets and perforated caps, filled initially with oxygen at room temperature and pressure of one atmosphere. The oxygen consumed was estimated by weighing the water required to restore the pressure to atmospheric after cooling the bottles containing the samples to room temperature.

The data for oxidations at 90° C are taken from an earlier work by the author¹.

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TRANSFORMATION BY THE ACTION OF HEAT AND OXYGEN OF THE SULFUR BONDS WHICH COMPOSE A VULCANIZATION NETWORK *

T. G. DEGTEVA AND A. S. KUZMINSKIĬ

We demonstrated earlier the existence of a process of joint oxidation of the solvent and the vulcanizate swollen in it¹. The oxidative destruction of swollen vulcanizates, where the testing conditions are equal, depends on the speed at which the peroxides are formed and decompose, not only in the rubber but in the solvent as well.

When swollen polybutadiene (SK-B) vulcanizates² are oxidized, two related and simultaneous processes occur, viz., destruction and structure formation. The solvent has no inhibiting effect on the latter process.

In the course of the oxidation of swollen vulcanizates, the destructive process can predominate only in the presence of an antioxidant; it is only after the exhaustion of the latter that the speed of structure formation in the vulcanizate equals or exceeds the speed of destruction.

The present work is a study of the influence which the sulfur bonds forming the vulcanizate network have on the oxidation of the vulcanizate in a swollen condition.

EXPERIMENTAL PART

The specimens studied consisted of four types of polybutadiene vulcanizates: (1) with tetramethylthiuram disulfide but no sulfur; (2) with sulfur and an ultra-accelerator (zinc ethylphenyldithiocarbamate); (3) with diphenylguanidine and sulfur; and (4) without sulfur or accelerator (a thermal vulcanizate). The vulcanizing conditions and the composition and properties of the original stocks are given in a previous communication.

Before the tests were made, the stocks were first extracted with a mixture of methanol and acetone for 50 hours in order to remove the antioxidants (Neozone-D, free sulfur, and accelerators and their decomposition products).

Oxidation of vulcanizates swollen in decalin at 150° C.—The swollen vulcanizates were not over 300 μ thick, and contained 0.2 gram of the rubber sample and 1.32 grams of solvent. Figure 1 shows curves of the kinetics of oxidation of all four types of stocks. The figure shows that the oxidation speeds of the swollen stocks rank in this order: thermal vulcanizate > thiuram vulcanizate > zinc ethylphenyldithiocarbamate vulcanizate.

It is known³ that the polysulfide combined sulfur can be separated by a sodium sulfite solution from a vulcanizate which has previously been extracted in order to remove the free sulfur. For this purpose, finely cut pieces of the sulfur vulcanizates were boiled in a solution of sodium sulfite in an atmosphere of nitrogen. The vulcanizate samples were then soaked for 3–4 hours in distilled water and washed with water and alcohol, so as to remove the sodium sulfite

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from the *Zhurnal Prikladnoi Khimii*, Vol. 29, No. 1, pages 90–97 (1956). The original gives no address of the authors.

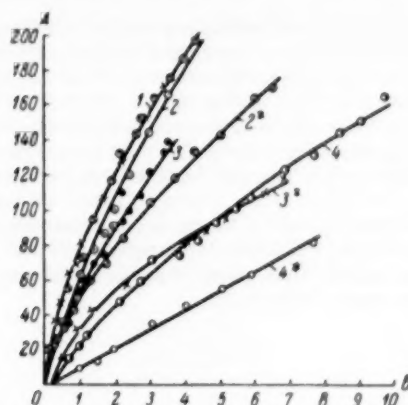


FIG. 1.—Influence of polysulfide sulfur on the kinetics of the oxidation of swollen vulcanizates. 1. Thermal vulcanizate. 2. Vulcanizate with tetramethylthiuram disulfide, after extraction and treatment with sodium sulfite. 2*. Tetramethylthiuram-disulfide vulcanizate after extraction alone. 3. Vulcanizate with zinc ethylphenyldithiocarbamate and sulfur, extracted and treated with sodium sulfite. 3*. The same, after extraction alone. 4. Vulcanizate with diphenylguanidine and sulfur, after extraction and treatment with sodium sulfite. 4*. The same, after extraction alone. The abscissa represents the time in hours; the ordinate the amount of oxygen absorbed in millimoles per mole of the rubber.

completely. After drying in a vacuum, the vulcanizates were oxidized in a swollen condition at 150° C.

The vulcanizates, though of different structures, all oxidized more rapidly after being boiled in the sodium sulfite solution than before this treatment. The kinetic curves for the oxidation of swollen stocks vulcanized with tetramethylthiuram disulfide and with zinc ethylphenyldithiocarbamate coincide almost exactly with the curve for the oxidation of a swollen thermal vulcanizate. The diphenylguanidine vulcanizate is an exception, however; it oxidizes fairly slowly in a swollen condition.

On the basis of the data obtained, we may assume that nearly all of the sulfur vulcanizates tested contain polysulfide sulfur. It is possible, however, that in vulcanizates of different types, the bonds have varying degrees of polysulfide content. A polybutadiene stock vulcanized with diphenylguanidine and sulfur forms polysulfide bonds to a greater extent than do vulcanizates of other types.

Data are given below on the sulfur removed from a diphenylguanidine vulcanizate by extraction with acetone. When a diphenylguanidine vulcanizate

TABLE I
KINETICS OF THE REMOVAL OF SULFUR FROM A STOCK
VULCANIZED WITH DIPHENYLGUANIDINE

Time of extraction (hours)	Amount of sulfur removed (per cent of the original vulcanizate weight)
50	1.820
100	1.892
150	1.944
200	1.971
250	1.978

is extracted for 250 hours and then boiled in a sodium sulfite solution for a period of 12 hours, the polysulfide sulfur removed from the vulcanizate amounts to about 3 per cent of its combined sulfur content. That is, approximately 9 per cent of the total polysulfide sulfur present in the vulcanizate is removed in this way. The data presented indicate that the sulfur bonds in diphenylguanidine vulcanizates are fairly unstable. From this data on oxidative degradation in vulcanizates, some conclusions can also be drawn as to the nature of the vulcanization itself.

A comparison of kinetic curves of the oxidation of swollen stocks which were vulcanized with zinc ethylphenyldithiocarbamate for 20 and 80 minutes at 90° C, and then extracted for 80 hours, shows that the 20-minute vulcanizate has a much lower oxidation speed (Figure 2).

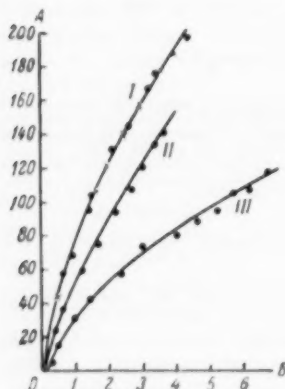


Fig. 2.—Influence of polysulfide sulfur on the kinetics of the oxidation of swollen stocks vulcanized with zinc ethylphenyldithiocarbamate and sulfur for different lengths of time. I. ●—Thermal vulcanizate; X—Stock vulcanized with zinc ethylphenyldithiocarbamate and sulfur for 80 minutes and then extracted. II. Stock vulcanized with zinc ethylphenyldithiocarbamate for 20 minutes and then extracted and treated with sodium sulfite. III. Stock vulcanized with zinc ethylphenyldithiocarbamate for 80 minutes and then only extracted. The abscissa represents the time of oxidation in hours; the ordinate the amount of oxygen absorbed in millimoles per mole of the rubber.

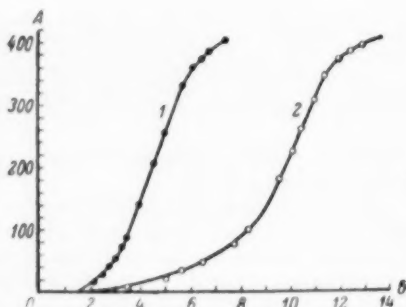


Fig. 3.—Influence of sulfur on the kinetics of the oxidation of the polybutadiene polymer at 90° C. 1. Without sulfur. 2. With 0.35 per cent sulfur added. The abscissa represents the time in hours; the ordinate the amount of oxygen absorbed in millimoles per mole of the polymer.

After the 20-minute vulcanizate is treated with a sodium sulfite solution, its kinetic curve of oxidation approaches the curves for the oxidation of the thermal vulcanizate and the 80-minute vulcanizate. These facts indicate that vulcanizates contain a larger number of polysulfide bonds in their earlier stages of vulcanization than they do later. As the vulcanization time lengthens, the sulfur bonds become rearranged more and more, and thereby the polysulfide content decreases.

A change of the polysulfide content of the bonds has an immediate effect on the speed of oxidation of the vulcanizate; the lower the polysulfide content, the more rapid is the oxidation reaction.

Oxidation of a polymer containing sulfur at 90° C.—We have shown⁶ that

when a sodium-butadiene polymer is oxidized in the presence of sulfur at 90°, an auxiliary structure-forming process arises (in addition to the structure formation with oxygen), which does not cease after the sulfur combines with the rubber. No thermal structure formation is observed under these conditions.

Figure 3 shows the influence of the sulfur on the kinetics of oxidation in the sodium-butadiene polymer at 90°. The figure shows that the introduction of sulfur into rubber causes a retardation of the oxidation, which is revealed by a slight lengthening of the induction period and a reduction of the speed of the autocatalytic oxidation reaction.

The antioxidant action of sulfur is related to its combination with the polymer during oxidation. The kinetics of sulfur consumption in the course of the

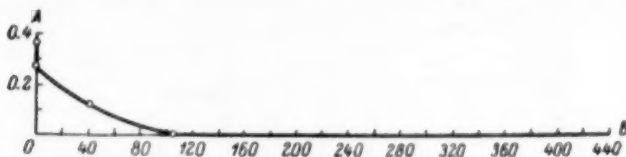


FIG. 4.—Consumption of sulfur in the process of oxidation of a polybutadiene polymer at 90° C. The abscissa represents the amount of oxygen absorbed in millimoles per mole; the ordinate the amount of free sulfur (in grams) remaining in one gram of the polymer.

oxidation reaction is shown in Figure 4; it is evident from this that at the point where 110 moles of oxygen are absorbed by one mole of polymer, no free sulfur remains in the system.

In spite of the absence of free sulfur from the rubber, the equilibrium concentration of stable peroxide compounds in all the latter stages of oxidation is continuously below their concentration in rubber oxidized without sulfur (Figure 5). After the sulfur has combined with the polymer, the unsaturation of the latter decreases more rapidly during the oxidation process than does that of the polymer without sulfur (Figure 6).

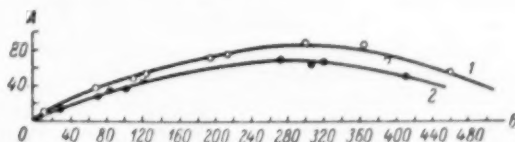


FIG. 5.—Accumulation of peroxides in the course of the oxidation of the polybutadiene polymer at 90° C. 1. Without sulfur. 2. With 0.35 per cent sulfur added. The abscissa represents the amount of oxygen absorbed in millimoles per mole of rubber; the ordinate the amount of oxygen present in the peroxide form, in millimoles per mole of the rubber.

In order to determine how the consumption of double bonds is distributed between the principal and side chains in the oxidation of a polymer with 0.35 per cent sulfur, a polymer sample containing 220 millimoles of combined oxygen per mole was ozonized. The ozonolysis data show that whereas the side chains of the original polymer contained 69 per cent of the double bonds, after oxidation they retained only 49.7 per cent.

Thus the loss of unsaturation in the side chains during the oxidation of the polymer containing sulfur amounted to 19.3 per cent. The difference in the total loss of unsaturation, determined iodimetrically, between an oxidized polymer with 0.35 per cent sulfur and one without sulfur (both containing 220 millimoles of oxygen per mole) equaled 20.0 per cent.

Thus the whole of the loss of unsaturation occasioned by the combination of sulfur with the polymer, and later by the development of a structure-forming reaction in the rubber, occurs among the double bonds in the side chains.

It is known⁶ that gaseous reaction products are formed when a sodium-butadiene polymer is oxidized. Table 2 gives data on the composition of the volatile products liberated during the oxidation of rubber containing sulfur.

The data of Table 2 show that the presence of sulfur in rubber causes a decrease of the amount of volatile products liberated by the reaction, although the quantitative ratio between formic acid and formaldehyde does not change.

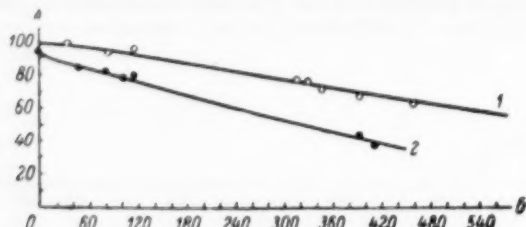


FIG. 6.—Decrease of unsaturation during the oxidation of the polymer at 90° C. 1. Without sulfur. 2. With 0.35 per cent sulfur added. The abscissa represents the amount of oxygen absorbed by the polymer in millimoles per mole; the ordinate the percentage of unsaturation.

These volatile products are produced mainly by the oxidative rupture of double bonds in the side chains of the rubber. The decrease of the quantity of volatile products formed in the oxidation of rubber when sulfur is present is due to the reaction between these bonds and sulfur. The behavior of sulfur in the above experiments seems to indicate that during the oxidation of rubber containing sulfur, the eight-membered sulfur ring opens, with subsequent formation of polysulfides. The polysulfide bonds formed probably decompose during the further oxidation of the rubber to liberate biradicals containing a variable number of sulfur atoms⁷.

TABLE 2
VOLATILE PRODUCTS FORMED BY THE OXIDATION OF
RUBBER CONTAINING SULFUR AT 90° C

Amount of sulfur added (per cent by weight)	Total oxygen content of volatile products (millimoles/mole of rubber)	Oxygen in HCOOH (millimoles/mole of rubber)	Oxygen in HCHO (milli- moles/mole)
0	154.6	49.7	104.9
0.35	97.46	35.18	62.27
0.35	94.94	37.8	57.14

The biradicals liberated by the polysulfide groups bring about a structure-forming (vulcanization) reaction, a decrease of the speed of the oxidation reaction and a decrease of the equilibrium concentration of stable peroxides in the rubber.

Decomposition of sulfur bonds in swollen vulcanizates heated in the absence of oxygen.—Kargin and Slonimskii have reminded us that it is possible for the sulfur bonds which form the vulcanizate network to be decomposed by the action of heat alone. Dogadkin and Tarasova⁸ have observed that polysulfide bonds in vulcanizates decompose under mechanical strains and at high temperatures.

We set up another set of experiments in order to determine to what extent the destruction of a polybutadiene vulcanizate is due to the decomposition of polysulfide bonds. The testing was done at 150°C , and the solvent was ethylbenzene. The solvent was purified of any traces of air and was measured into ampoules by the apparatus shown in Figure 7. The ethylbenzene was distilled in a weak stream of purified nitrogen at $26\text{--}28^{\circ}\text{C}$, in a vacuum of 10^{-3} mm. of mercury. Before the distillation, purified nitrogen was bubbled through the solvent for 3 hours.

The solvent was transferred, by means of recondensation under a vacuum of 10^{-7} mm. of mercury, from receiver 1 to trap 2, which was immersed in a cooling bath containing acetone and dry ice. Stopcock 3 was then closed and the cooling liquid was removed, after which the trap containing the solvent was heated

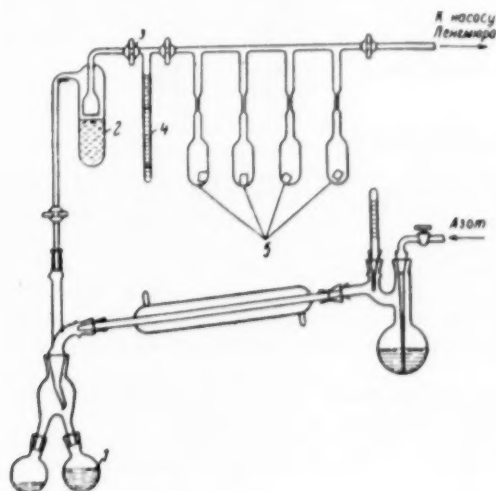


Fig. 7.—Diagram of apparatus used for distilling and measuring the oxygen-free solvent. 1. Receiver. 2. Trap. 3. Stopcock. 4. Graduated measuring tube. 5. Ampoules containing rubber samples. The arrow at the top indicates the vacuum pump; the one at the bottom the direction of the flow of nitrogen.

on a water bath at 30°C for 10 minutes and then cooled again with the mixture of acetone and dry ice. This operation was repeated three or four times in such a way that after each operation any traces of air removed from the solvent were taken off by the vacuum pump. Then a portion of the solvent was transferred by vacuum to the graduated measuring tube 4, from which 1.5-ml. portions of the ethylbenzene were measured into ampoules immersed in a cooling bath. These ampoules already contained samples of the vulcanizate, swollen to a known maximum degree.

If no air was given off when the solvent in the ampoule was heated and cooled three times, the ampoule was sealed and placed in a constant-temperature oven at 150°C for a given length of time. After the ampoule was heated, it was cooled with dry ice and opened, and the ethylbenzene was evaporated in a vacuum. After the solvent was removed, the vulcanizate samples were swollen in benzene, and the maximum swelling was determined with a torsion balance. The results are shown in Table 3.

TABLE 3
DETERMINATION OF MAXIMUM SWELLING OF VULCANIZATE
SAMPLES IN BENZENE*

Type of vulcanizate	Weight of vulcanizate (grams)	Heating time (hours)	Maximum swelling (per cent)	
			Before heating	After heating
Thiuram vulcanizate	0.040	2	565	600
	0.023	4	560	604
	0.034	6	555	608
	0.021	8	570	615
Diphenylguanidine-sulfur vulcanizate	0.265	5	420	1230
	0.0195	9	450	1020
	0.036	10	485	1200
	0.0365	22	485	1132
Thermal vulcanizate	0.023	3.5	700	720
	0.028	7.25	450	450
	0.031	10	450	459

* The quantity of solvent was 1.5 grams.

The experimental data indicate that when swollen vulcanizates are heated in a high vacuum, only the longer polysulfide bonds undergo decomposition; the carbon and monosulfide crosslinks are not altered materially. Heating a diphenylguanidine vulcanizate at 150° without a solvent and in the absence of oxygen causes a reduction of the maximum swelling from 450 to 310 per cent. If a stock vulcanized with diphenylguanidine and sulfur is extracted and placed in hydrazine hydrate for 14 hours, its modulus⁹ rises from 14 to 18 kg. per sq. cm.

Thus in both cases decomposition of the polysulfide bonds results in the formation of an additional number of crosslinks. These facts also attest to the mobility of the sulfur in the polysulfide bridges of the vulcanizate whose structural network was formed with diphenylguanidine and sulfur.

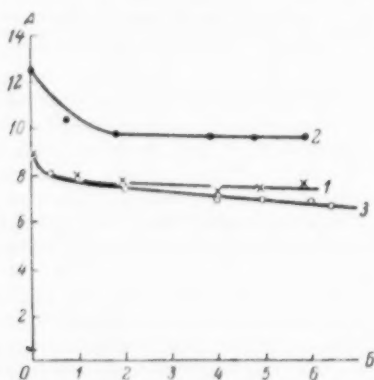


FIG. 8.—Change of the conditional equilibrium high-elastic modulus E_e in extracted vulcanizates heated in an atmosphere of nitrogen at 100° C. 1. Vulcanizate with tetramethylthiuram disulfide. 2. With zinc ethylphenyldithiocarbamate and sulfur. 3. With diphenylguanidine and sulfur. The abscissa represents the time in hours; the ordinate the equilibrium modulus E_e in kg. per sq. cm.

In another set of experiments we used the change of equilibrium modulus as a means of studying the behavior of sulfur bonds in vulcanizates of different types at 100° C in an atmosphere of nitrogen (Figure 8). Only the diphenylguanidine vulcanizate gives a slow steady decrease of modulus; this is due to rupture of the polysulfide bonds at 100° C.

Dogadkin and Tarasova⁷ have shown that natural-rubber stocks vulcanized with diphenylguanidine and sulfur or with sulfur alone undergo an almost complete loss of stress at 100° C.

The slight decrease of the modulus of a polybutadiene stock vulcanized with diphenylguanidine and sulfur is probably due to the existence of a structure-forming process brought about by the biradicals which are liberated by the polysulfide bonds and contain varying numbers of sulfur atoms. Further, in stretched polybutadiene vulcanizates a complete loss of stress is impossible in principle, since the carbon bonds formed, which are characteristic of this type of vulcanizate, cannot be broken under the conditions of the test.

CONCLUSIONS

1. A study of the effect of combined sulfur on the oxidation of swollen and unswollen polybutadiene vulcanizates shows that stocks vulcanized with different types of accelerators (tetramethylthiuram disulfide, diphenylguanidine, and zinc ethylphenyldithiocarbamate) form sulfur bonds which differ in their content of long polysulfide groups.

2. It is shown that sulfur liberated by the polysulfide bonds in vulcanizates reduces the speed of the oxidation reaction and the equilibrium concentration of stable peroxides. The sulfur content also governs the structure-forming process which develops when a raw polymer containing sulfur is oxidized at 90° C. The decomposition products of the polysulfide groups likewise lower the speed of oxidation in swollen vulcanizates at 150°.

3. When swollen vulcanizates are heated in the absence of oxygen at 150°, only the polysulfide bonds decompose. Heating unswollen vulcanizates under the same conditions, however, brings about the reverse effect, viz., structure formation.

4. Sodium sulfite and alcoholic alkali do not remove completely the polysulfide sulfur from vulcanizates.

5. In the process of vulcanization a rearrangement of the sulfur bonds takes place, and this is accompanied by a reduction of the polysulfide content.

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ROLE OF PARTICLE DIAMETER AND LINKAGE FORMATION IN RUBBER REINFORCEMENT

A. F. BLANCHARD

DUNLOP RESEARCH CENTRE, BIRMINGHAM

INTRODUCTION

The reinforcement of rubber, as judged by improved tensile strength, tear, and abrasion resistance is very dependent on the particle diameter of the reinforcing filler. However, the number and size of the particles seem unlikely to be the only factors of importance; and there is in fact some evidence for this. The following contribution to the subject is concerned with interpreting the action of carbon blacks in stiffening and improving the abrasion resistance of rubber, though other aspects also will be briefly considered.

Reinforced rubber can be softened drastically by pre-extensions exceeding the extension used to determine the modulus (cf. Mullins¹; Blanchard and Parkinson²). The stress-strain curves for extensions less than the pre-stress² and between 70 and 400 per cent, can then be described by the following equation:

$$\ln F - \phi(\alpha) = \ln G + \mu(\alpha - 1)^4 \quad (1)$$

where F is the stress (kg./cm.²) for some extension ratio α on the fourth extension, i.e., after three successive applications of the pre-stress S . The function $\phi(\alpha)$ depends only on the extension in accordance with the equation:

$$\phi(\alpha) = 0.31 (\alpha - 1) + \ln 1.62 [1 - 1/\alpha^2] \quad (2)$$

The parameters G and μ have been termed modulus and extension factor respectively, and both decrease as the pre-stress increases.

The extension factor μ expresses approximately the deviation from the theoretical equation of Guth and James³, representing unreinforced vulcanizates at moderate extensions. The parameter G will clearly reflect changes in rubber-filler linkages, and it has been used as a rough measure of stiffening linkages which have survived pre-stressing, including primary sulfur crosslinks formed during the vulcanization process. The practical value of this assumption as a working hypothesis has been fully demonstrated by Blanchard^{2,4} *et al.*, though it is without rigorous theoretical justification. On this basis a concept of force per linkage factor X due to pre-stressing was developed (see Blanchard *et al.*²), and hence the idea of linkage strength factor as the value of X when breakage occurs. This quantity X is a function of the pre-stress S , corresponding extension ratio α , and corresponding or residual modulus G , and is calculated from $X = \alpha S/G^{\frac{1}{4}}$. It can be related to the mechanical energy dissipated in breaking the linkages, as measured by a planimeter from the stress-strain curves⁴.

* Reprinted from the *Proceedings of the Third Rubber Technology Conference*, London, 1954, pages 592-608.

A general law of softening corresponding to a common linkage strength distribution parameter $K = 0.276$ for the secondary linkages formed by a variety of types and grades of filler is expressed² by the equations:

$$G = G^* + G_r F(X) \quad (3)$$

$$F(X) = \frac{K^2}{4} \int_x^\infty X^4 e^{-KX^4} dX \quad (4)$$

where G^* is the residual modulus determined by strong linkages, which include those due to vulcanization. They are here termed primary to distinguish them from the secondary linkages G_r which can be readily broken by pre-stressing. It has been shown that X does not require correction to take account of the volume occupied by the filler, but values of G^* and G_r should be multiplied by $1 + V$ where V is the volume of filler per unit volume of rubber⁴.

EXPERIMENTAL

The experimental methods used to study stress-strain behavior have been described elsewhere by Blanchard² *et al.* In the early experiments values of G_r and G^* were obtained from the slope and intercept respectively of graphs of G versus the function $F(X)$ for a range of pre-stresses between 30 and 200 kg./cm.², and with separate testpieces for each pre-stress. Later the procedure was replaced by an abbreviated technique which employed only two magnitudes of pre-stress (40 and 140 kg./cm.²). Both pre-stresses were applied to the same testpiece, the effect of the preceding 40 kg./cm.² on the measurement for 140 kg./cm.² being negligible because of its relatively small value. The procedure for obtaining G and μ also was shortened by considering only two well-spaced points on the fourth extension curve. Thus, if F_1 and F_2 are the stresses corresponding to extension ratios α_1 and α_2 , we have by Equation (1):

$$\begin{aligned} \ln F_1 - \phi(\alpha_1) &= \ln G + \mu(\alpha_1 - 1)^4 \\ \ln F_2 - \phi(\alpha_2) &= \ln G + \mu(\alpha_2 - 1)^4 \end{aligned}$$

Subtracting and denoting $\ln F - \phi(\alpha)$ by Y we obtain

$$\mu = \frac{Y_2 - Y_1}{r} \quad (5)$$

where

$$r = (\alpha_2 - 1)^4 - (\alpha_1 - 1)^4 \quad (6)$$

Hence the modulus G can be obtained from the relation

$$G = \ln^{-1} (Y_1 - \mu A) \quad (7)$$

in which A has been written for $(\alpha_1 - 1)^4$. A table was constructed giving the percentage elongations corresponding to suitable values of α_1 and α_2 to be used according to the extension at the third pre-stress. This table included the corresponding values of $\phi(\alpha)$, r , and A . The moduli G_1 and G_2 were obtained after pre-stresses 40 and 140 kg./cm.², the corresponding values X_1 and X_2 or $X = \alpha S/G^1$ were calculated, and hence $F(X_1)$ and $F(X_2)$. Equation 3 was then used to calculate G^* and G_r , using the mean data for four testpieces.

Thus:

$$G_r = \frac{G_1 - G_2}{F(X_1) - F(X_2)} \quad (8)$$

$$G^* = G_1 - G_r F(X_1) \quad (9)$$

Abrasion resistance indexes of the reinforced vulcanizates in these experiments were obtained using a constant power Lambourn machine (see Powell and Gough⁵). These are the reciprocal of the ratio of the weight loss by abrasion to the loss in weight of standard testpieces under conditions of constant power transmission.

The general formula for all the compounds to be tested in these experiments was (in parts by weight):

Natural rubber	100.0
Filler	Various
Stearic acid	2.0
Zinc oxide	5.0
Accelerator (N-cyclohexyl benzthiazole-2-sulfenamide)	Various
Sulfur	2.5
Antioxidant	1.0

All the compounds were mill mixed at low temperatures (initial roll temperature $60 \pm 5^\circ \text{C}$).

The experiments included a study of the changes in G_r and G^* with increasing concentrations of MPC and P33 blacks, Philblack A, calcium carbonate (Calcene), and magnesium carbonate. The formulas were basically as above with 0.5 part of accelerator with Philblack A, 0.7 part with magnesium carbonate, P33 black, and Calcene, and 0.8 part with MPC. Vulcanization periods were, respectively, 30 and 65 minutes at 280°F (138°C) for the P33 and MPC compounds, 30 minutes in the case of magnesium carbonate and Calcene, and 55 minutes for Philblack A. In the case of Philblack A, magnesium carbonate, and Calcene, the compounds were tested using the abbreviated technique for obtaining G_r and G^* .

Later the action of several fillers in rubber was compared after mill mixing to the above general formula. The fillers studied were HPC, MPC, and conductive channel blacks; graphitized channel black (Graphon); HAF, FF, and SRF blacks; lamp and Shawinigan blacks; and calcium silicate of small particle diameter (about 30 μ). The compounds contained 0.5 part by weight of accelerator, except in the case of calcium silicate, Graphon, HPC, MPC, and conductive channel blacks, which all had 0.7 part. In each case the volume concentration of filler per unit volume of rubber was $V = 0.26$, and the testpieces for all the tests, which included abrasion resistance, tear resistance and tensile strength, were vulcanized for 55 minutes at 280°F (138°C). The abbreviated pre-stress technique using pre-stresses 40 and 140 kg./cm.^2 , was employed in the stress-strain measurements. Duplicate mixings were prepared of all the compounds in the comparison.

An experiment to investigate the effect of pre-stressing on abrasion resistance also was carried out on some of the above compounds. Large dumb-bell shaped testpieces were pre-stressed, and the center portions were cut out and fixed to abrasion wheels for testing. The re-formation of secondary linkages in the interval at 20°C between pre-stressing and testing was negligible. Owing to breaking of the testpieces at the shoulder, pre-stresses greater than 150 kg./

cm.² were not used. Four testpieces were used for each pre-stress, two testpieces being formed from each of the duplicate mixings.

LINKAGE FORMATION AS REFLECTED BY STRESS-STRAIN MEASUREMENTS

In general the vulcanizates compared during the course of this investigation were given roughly the optimum time of cure, but it was decided that some study should be made of the effects on G_r and G^* of vulcanizing for times less than and greater than the optimum. Figure 1 shows values of G_r and G^* obtained by the abbreviated procedure for a range of cure times between 30 and 80 minutes at 280° F (138° C), the compound formulas being as on page 1286, with 50 parts by weight of MPC black, and 0.8 part of accelerator. The results

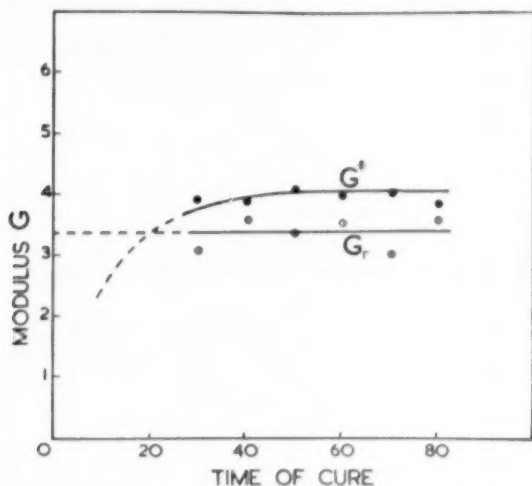


Fig. 1.—Effect of time of cure on G_r and G^* for a vulcanizate containing MPC black.

are not very sensitive to variations in the periods of vulcanization covering a considerable range on either side of the optimum in the region of 50 minutes. The dotted lines are to indicate the kind of trend which might be expected for short cures.

To obtain an idea of the variability of comparisons using the abbreviated method of testing and analysis the technique was applied to eight compounds of the same formula (HAF black 50, accelerator 0.5, in the formula on page 1286), but mill-mixed and vulcanized separately, the time of cure being 55 minutes at 280° F. The standard deviations under these conditions were respectively 0.21 on G^* and 0.24 on G_r .

Effect of increasing concentration of various fillers.—When no filler is present there is still an appreciable though relatively small degree of softening of the rubber by pre-stressing. If this is expressed roughly by the mathematical form (Equation 3) used for reinforced rubber, as a useful though not very accurate approximation, then $G_r = b \approx 0.9$. A component of G_r , for reinforced vulcanizates amounting to about $b = 0.9$ should therefore be allowed roughly to account for the softening of the rubber matrix itself⁴. The value of G_r corrected

for the volume occupied by the filler is $(1 + V)G_r$, where V is the volume of filler per unit volume of rubber; and the component of the secondary linkages due to the filler is $(1 + V)G_r - b^*$. This measure of secondary rubber-filler linkages has been plotted against the volume concentration V in Figure 2 for MPC and P33 black, and in Figure 3 for Philblack A, magnesium carbonate, and Calcene. The increase in secondary rubber-filler linkages with increasing concentration of filler is roughly linear up to $V = 0.3$ with the exception of the case of magnesium carbonate. A linear relation is not unexpected on the assumption that the ordinate of Figures 2 and 3 is a measure of secondary linkages induced by filler particles, and provided that the dispersion of these particles in the rubber does not vary with the concentration.

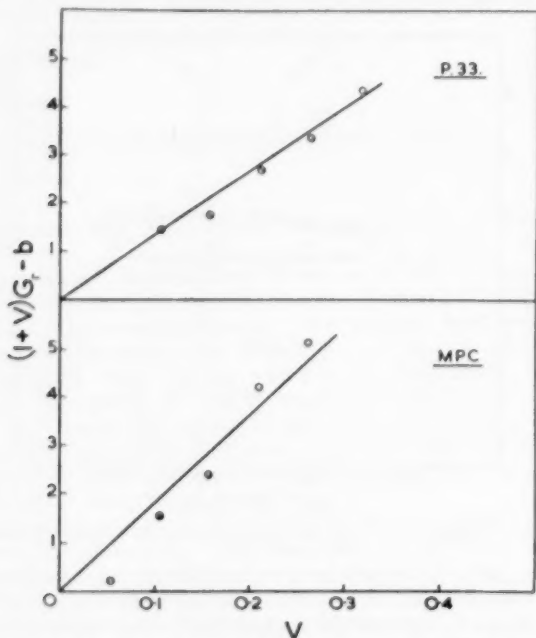


Fig. 2.—Increase in secondary linkages with concentration of filler.

The increase with filler concentration in the strong (primary) linkages represented by $(1 + V)G^*$ is shown in Figure 4 for MPC black, P33 black, and Calcene, and in Figure 5 for Philblack A. There is evidence of a decrease in $(1 + V)G^*$ with increasing concentrations of magnesium carbonate. Figure 4 clearly shows the marked increase in primary linkages on incorporating MPC black, and the relatively small increase with P33 black, and even smaller increase with Calcene. A common value $G^* = 3.7$ for the intercept at zero concentration appears consistent with results for gum stocks of similar formula. In comparing various fillers (see below), this has been subtracted in order to obtain a rough estimate of strong linkages contributed by the filler. The difference between MAF black (Philblack A), which is responsible for a marked increase in strong linkages, and magnesium carbonate, with no ability to form

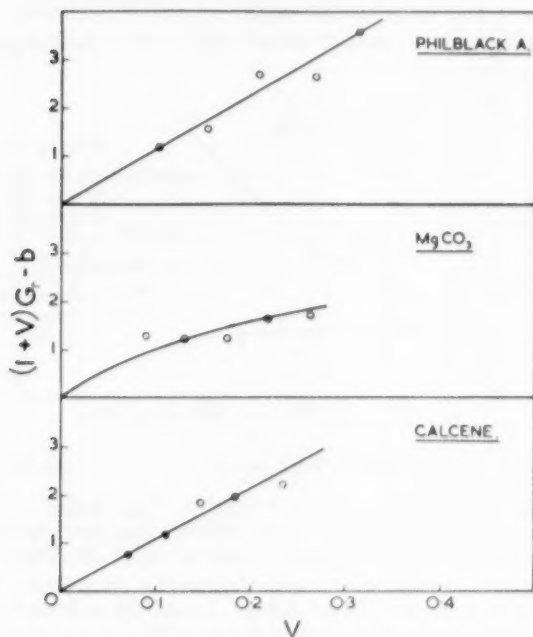


FIG. 3.—Increase in secondary linkages with concentration of filler.

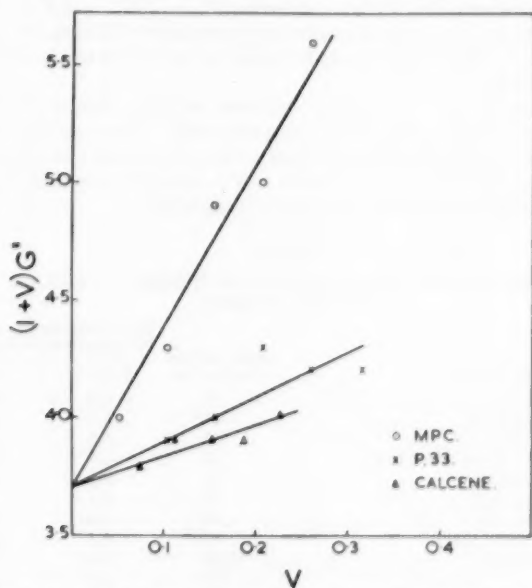


FIG. 4.—Increase in strong (primary) linkages with concentration of filler.

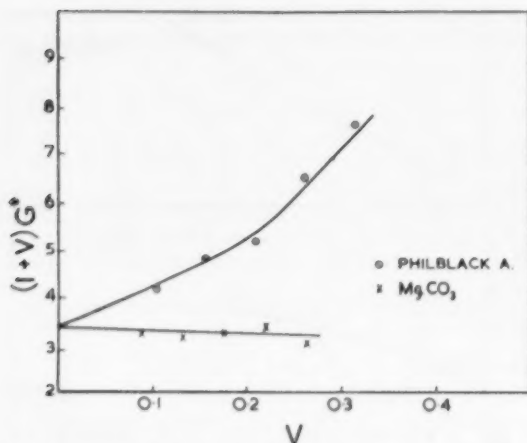


Fig. 5.—Increase in strong (primary) linkages with concentration of filler.

strong linkages, is well illustrated by Figure 5. The increase due to MAF black in this case appears to become more rapid at high concentrations.

Comparison between fillers.—Table I shows the mean estimates of strong or primary linkages $(1 + V)G^*$ which were obtained for the duplicate mixings in the experiment to compare various fillers. Estimates of secondary linkages $(1 + V)G_r$, and the energy dissipated in breaking them, are presented and discussed elsewhere⁴. The component G_r^* of the primary linkages due to the filler is roughly represented by the expression $(1 + V)G^* - 3.7$ in which 3.7 is taken to represent similar vulcanizates without filler. Estimates by the electron microscope of the arithmetic mean particle diameters of the fillers also are quoted in the table.

The table shows no relationship between particle diameter and primary linkages as reflected by stress-strain measurements. The partially graphitized channel black (Graphon) shows drastically reduced linkage forming capacity in comparison with normal carbon blacks. It is doubtful whether any primary linkages are contributed by the calcium silicate filler.

TABLE I
STRESS-STRAIN DATA FOR NATURAL RUBBER CONTAINING
VARIOUS FILLERS

Type of filler	Mean particle diameter, mμ	Primary linkages as reflected by stress-strain measurement	
		$(1 + V)G^*$	$(1 + V)G^* - 3.7$
Conductive channel black (Spheron C)	23	4.8	1.1
HPC black (Spheron 4)	24	5.3	1.6
MPC black (Spheron 6)	25	5.6	1.9
Graphitized MPC black (Graphon)	25	4.2	0.5
HAF black (Vulcan 3)	27	6.1	2.4
FF black (Sterling 105)	32	5.1	1.4
FF black (Sterling 99)	39	5.4	1.7
Shawinigan acetylene black	40	6.1	2.4
SRF black (Sterling 8)	80	5.5	1.8
Lampblack	100	5.5	1.8
Calcium silicate	≈30	3.9	0.2

TABLE II
REINFORCEMENT DATA FOR VARIOUS FILLERS IN NATURAL RUBBER

Type of filler	Mean particle diameter, μ	Abrasion resistance	A.S.T.M. tear resistance at 20° C		Tensile strength, kg./cm. ²
			With grain	Against grain	
Conductive channel black (Spheron C)	23	110	42.4	45.7	244
HPC black (Spheron 4)	24	117	45.2	42.8	252
MPC black (Spheron 6)	25	110	36.3	41.1	254
Graphitized MPC black (Graphon)	25	74	29.7	30.9	220
HAF black (Vulcan 3)	27	116	40.5	41.1	242
FF black (Sterling 105)	32	87	39.7	38.7	228
FF black (Sterling 99)	39	74	37.9	35.8	239
Shawinigan acetylene black	40	78	32.2	35.3	206
SRF black (Sterling 8)	80	52	26.5	23.3	201
Lampblack	100	41	21.6	17.8	188
Calcium silicate	≈ 30	24	18.4	18.0	179

REINFORCING ACTIVITY OF FILLERS

Table II shows further data on the physical properties of the compounds represented in Table I. The importance of filler particle diameter in determining the reinforcement of rubber is generally appreciated, and it is well illustrated by these data. The partial graphitization of channel black to form Graphon has reduced its reinforcing activity substantially. The calcium silicate

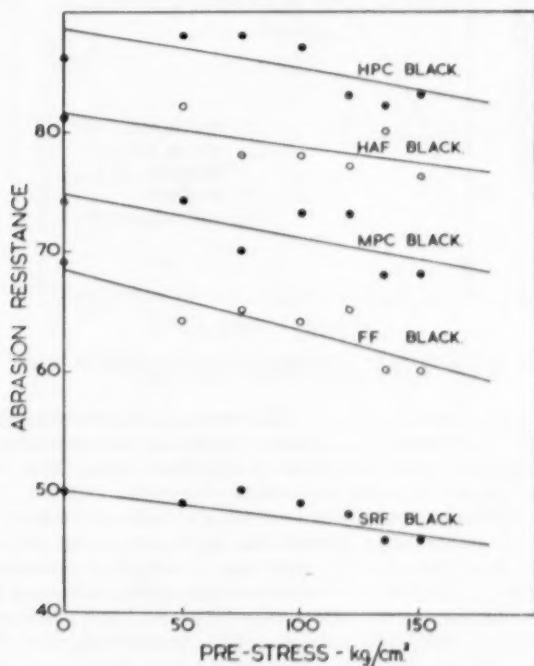


FIG. 6.—Effect of pre-stresses 0 to 150 kg./cm.² on abrasion resistance.

has little reinforcing ability, although the particle diameter is in the region of 30 $m\mu$.

DISCUSSION

Contribution of linkages to reinforcement.—In previous work only minor importance in reinforcement was attributed to those weak (secondary) linkages induced by fillers which can be readily broken by pre-stressing, though evidence was presented of some reduction in abrasion resistance by pre-stressing (see Blanchard² *et al.*). This conclusion is supported by later investigations which show no prospect of explaining differences in reinforcing ability by considering particle diameter together with either the secondary linkages or the

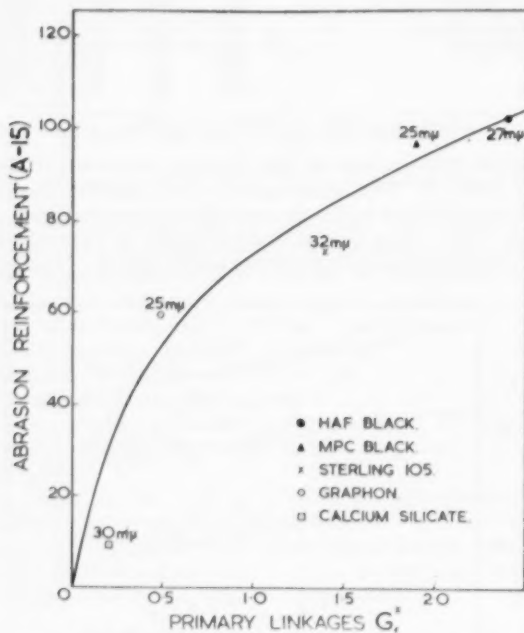


Fig. 7.—The dependence of abrasion reinforcement on primary linkages induced by fillers of similar particle size.

energy dissipated in breaking them⁴. Moreover, a more extensive investigation of the effect of pre-stressing on abrasion resistance indicates that the earlier experiments exaggerated the magnitude of the effect, though it is not clear how this happened. Figure 6 shows the results of the later experiments described on page 1287. The abrasion resistance indexes are all considerably lower than those in Table II, and this may be due, at least in part, to the period of 8 to 12 months aging before testing. The reduction in abrasion resistance with pre-stresses up to 150 kg./cm.² is quite small, and shows little difference between the various carbon blacks tested. Regression analysis gave negative slopes of magnitudes 0.036, 0.030, 0.037, 0.052, 0.027, respectively for HPC, HAF, MPC, FF, and SRF blacks. The experiment was repeated on a freshly mixed and therefore unaged HAF vulcanizate, and this also showed little decrease in

abrasion resistance with pre-stresses up to 150 kg./cm.², but the abrasion resistance was roughly 20 per cent higher than that of the aged HAF vulcanizate. These results come closer than previous work to the results obtained by the Research Association of British Rubber Manufacturers (Research Memorandum R352) which indicated no effect of pre-stressing on abrasion resistance.

The abrasion resistance with $V = 0.26$ volumes of a filler which acts merely as a diluent would be expected to be reduced by the presence of the filler. Data for inert fillers of large particle size suggest an abrasion resistance index A between 15 and 20 for $V = 0.26$, and this can be taken for comparison with the data in Table II for reinforcing fillers. With no filler present ($V = 0$) the abrasion resistance A_0' would be in the region 20 to 25. In Figure 7 the value

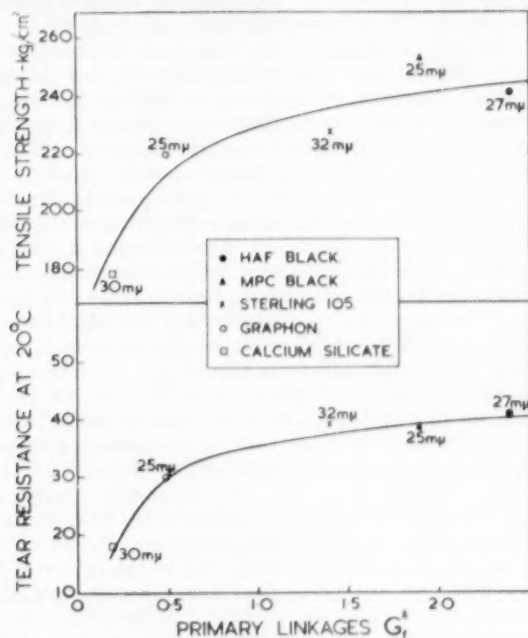


FIG. 8.—The dependence of tear resistance and tensile strength on primary linkages induced by fillers of similar particle size.

$A_0' \approx 15$ when $V = 0.26$ has been taken for an inert filler in order to plot the increase $A - A_0'$ due to reinforcing activity against the primary linkages $G_f^* = (1 + V)G^* - 3.7$ introduced by fillers of similar mean particle diameters in the region 25 to 30 μ. The graph clearly shows a correlation for a given particle diameter between abrasion resistance and primary linkages as reflected by stress-strain measurements. The stress-strain data in Figure 7 for the calcium silicate filler, and in Figures 4 and 5 for Calcene and magnesium carbonate, show that these fillers with little effect on abrasion resistance, differ further from carbon blacks in having little or no tendency to introduce some form of strong-type linkage. The graphs in Figure 8 of tear resistance and tensile strength against primary linkages are broadly similar to Figure 7. It can be concluded that primary linkage formation by carbon blacks does make a vitally

important contribution to reinforcement. On the other hand Figure 7 indicates that abrasion resistance is not very sensitive to the number of primary linkages in the quantities normally obtained with carbon blacks, much of the improvement being retained even with the partially graphitized black known as Graphon, which shows greatly reduced capacity to form linkages. Figure 8 shows that this conclusion applies with even greater emphasis to tensile strength and tear resistance. A much smaller number of primary linkages than is normally introduced by carbon blacks can evidently contribute much to the reinforcement of rubber if the filler particles are small.

Effect of carbon particle diameter on reinforcement.—The predominating influence of particle diameter on tensile strength, tear, and abrasion resistance is illustrated by the data in Table II. This paper is primarily concerned with reinforcement as measured by abrasion resistance, and only that property is considered here. It may be suggested that the poor reinforcement with coarse blacks of low specific surface is due to the relatively low interfacial area for linkage formation. However, when blacks of different particle sizes are compared by stress-strain measurements, the primary linkage formation as reflected by these data (Table I) is unrelated to particle diameter, and so could not explain the effect of particle diameter on reinforcement. A study of the secondary linkages, moreover⁴, has shown that the filler particle diameter had no influence in these experiments on the energy dissipated in breaking secondary linkages, or their number as reflected by their stiffening action. This may be considered a serious objection to the presumption that specific surface or interfacial area determines linkage formation in rubber, and hence (supposedly) the reinforcement. The impossibility of attributing the dependence of reinforcement on particle diameter to differences in the interfacial areas ostensibly available for primary linkage formation can also be seen by reference to Figure 7. This graph shows the variation of abrasion reinforcement ($A-15$) with primary linkages as reflected by stress-strain data for fillers of similar particle diameter. It indicates that even as little as one-third of the primary linkages induced by HAF black provides an abrasion reinforcement of about 70 for equivalent particle size, whereas Table II shows that SRF black with roughly one-third the specific surface provides roughly three-quarters of the primary linkages and an abrasion reinforcement of only 37. Moreover, any theory of reinforcement based on the concept of total surface available to the rubber suffers from the objection that it implies increasing reinforcement with diminishing particle diameter, no matter how small the particles. This is difficult to accept because it suggests that chemical crosslinking by molecules (e.g., sulfur) would be the best means of reinforcement, whereas all our experience suggests that incorporation of small filler particles is necessary to obtain a large improvement in abrasion resistance. For good wear resistance the particles, though small, probably need to have macromolecular dimensions.

Role of particle diameter and linkage formation in reinforcement.—For a given dispersion and concentration of filler it is suggested that reinforcement is most likely to find proper expression in terms of the number of linkages per particle and the number of particles. This is as natural an assumption as any which could be made concerning reinforcement; and it is in agreement with the conclusion that particle diameter is of major importance on its own account, and not through influencing the degree of linkage formation. A decrease in the particle diameter d has opposed effects in increasing the number of particles, N , per cc. of rubber and filler, and reducing the number of linkages, u , per particle. Consequently there is no reason why the above concept should not be consistent

with the conclusion that reinforcing particles probably need to have macromolecular dimensions, though small. This concept interprets reinforcing action in terms of two variables, u and N , the particular functions describing its dependence on each of these quantities being as yet unspecified. It would be equivalent to an interpretation in terms of specific surface only if the influence of these two quantities could be expressed in terms of their product Nu ; and if the number of linkages u per particle were proportional to the particle surface area d^2 , so as to make the product proportional to $1/d^3 \times d^2$, i.e., to the specific surface.

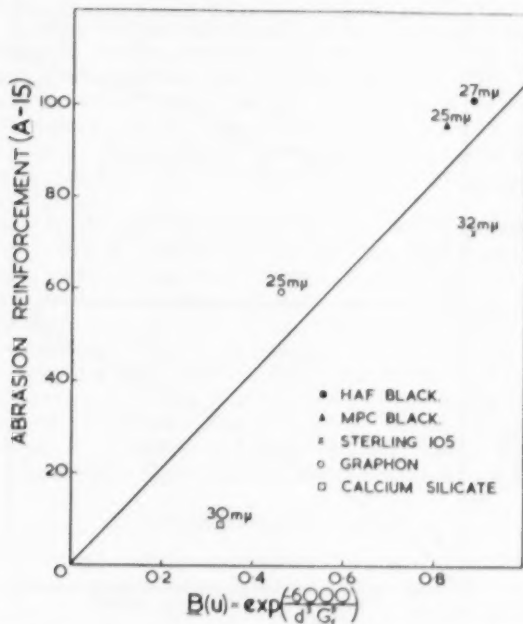


FIG. 9.—Relation between abrasion reinforcement and primary linkages per particle for fillers of similar particle size.

The next step in developing these ideas was to recognize that the characteristics of the rubber itself, and the proportion of rubber present, must limit the abrasion reinforcement ($A - A'$) which can be obtained by the inclusion of active filler particles. This limit will be denoted by Q_s when the volume of filler per unit volume of rubber is V . It will also be assumed that the dependence of reinforcement on u and N can be expressed by separate functions, so that:

$$A - A_s' = Q_s B(u) E(N) \quad (10)$$

where $B(u)$ is some function of the number of linkages per particle, and $E(N)$ is some function of the number of particles. When there are no primary linkages per particle, i.e., $u = 0$, we would expect no reinforcement, and $B(u) = 0$. When the concentration of filler and the particle diameter are constant, we have $E(N) = \text{constant}$; and this is roughly the condition applying to Figure 7,

which describes the influence of primary linkage formation on the abrasion reinforcement ($A - A_v'$) for $V = 0.26$ and $A_v' = 15$.

To fit the curve in Figure 7 a function is proposed for trial having the form

$$B(u) = \exp(-\tau/u) \quad (11)$$

where τ is some constant. This relationship gives $B(u) = 0$ when $u = 0$ and $B(u) \rightarrow 1$ as $u \rightarrow \infty$. The number of particles $(1 + V)N$ per cc. of rubber is $6V/\pi d^3$ so that the number of linkages u per particle is proportional to $d^3 G^* f / V$,

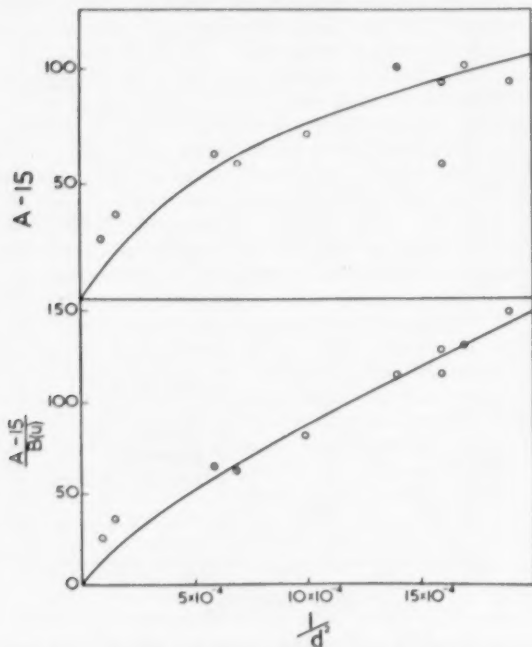


FIG. 10.—The dependence of abrasion reinforcement on the carbon particle diameter d and function $B(u)$ of the number of linkages per particle.

where $G^* f$ is the measure obtained from stress-strain data of primary linkages due to fillers (see p. 1287). Equation (11) may therefore be written:

$$B(u) = \exp(-\Gamma V/d^3 G^* f) \quad (12)$$

where Γ is some constant. If an expression of this form is consistent with the experimental data there should be a linear relation between the abrasion reinforcement data in Figure 7 and the function $B(u)$ as expressed by Equation (12). The graph in Figure 9 shows that there is a roughly linear relationship for these data with $\Gamma V = 6 \times 10^3$ when the particle diameter is expressed in $m\mu$. The value of ΓV was chosen also to obtain the best representation of the remaining data for carbon blacks of widely different particle size. Since $V = 0.26$ the value of Γ in this case is 2.3×10^4 .

The extent to which the function $B(u)$ expresses the influence of primary linkages on abrasion reinforcement by carbon blacks of widely different particle sizes can be seen in Figure 10. The upper curve represents abrasion reinforcement (see Table II) graphed as a function of the particle diameter only, and it shows considerable scatter of the points about the curve. In the lower curve differences in primary linkage formation have been taken into account by dividing by $B(u)$, and as a result a fairly smooth line is obtained. The form of the lower curve is that of the as yet unspecified function $E(N)$ in Equation (10). The significance of the choice of the reciprocal of d^2 in plotting the graphs is explained below.

The way in which the number of particles can be expected to influence abrasion reinforcement can be appreciated by picturing one layer being rubbed, torn, and split away from the body of the material. The linkage-forming particles closely involved by the separation will have their centers lying within a distance $d/2$ on either side of the line of cleavage, i.e., within a volume d if unit areas are separated. The number of particles closely involved by the rupture will therefore be Nd , which is proportional to the reciprocal of d^2 for a given concentration of filler.

At this stage no attempt will be made to assign a mathematical form to the function $E(N)$. This is because it is felt that the data presented are inadequate even for a tentative empirical choice. The function $B(u)$ of the number of linkages per particle (Equation 12) decreases very sharply as the particle diameter d decreases below 15 $m\mu$ to 10 $m\mu$ or less. It is therefore probable that the effect of diminishing numbers of linkages per particle will rapidly become the decisive factor for mean particle diameters in the region 15 to 10 $m\mu$. Consequently a sharp optimum or peak reinforcement in the region 20 to 10 $m\mu$ is indicated by extrapolation of the tentative empirical function $B(u)$. In practice, however, the sharpness of such an optimum would be reduced by the existence of a distribution of particle sizes about the mean in all practical cases.

GENERAL CONCLUSIONS

There are grounds for thinking (compare Blanchard² *et al.*, Parkinson⁶) that a relatively small number of strong linkages induced by carbon particles are an important factor in the reinforcement of rubber by carbon blacks. The evidence here presented of strong (primary) linkages from stress-strain measurements is practically confined to carbon blacks; and it is very noticeable, indicating substantial numbers with normal blacks, though few relative to the secondary linkages broken by pre-stressing. Abrasion resistance is not very sensitive to primary linkages in these quantities, a large part of the reinforcement being contributed by relatively few primary linkages such as are induced by Graphon.

For a given dispersion and concentration of filler it is suggested that reinforcement is most likely to find proper expression in terms of the number of particles and the number of linkages per particle, both factors being functions of the particle size. One consequence of this theory is a limit to the advantage which can be obtained by using smaller particles, and in this connection it is noteworthy that experiments with ultra-fine blacks have so far proved rather disappointing.

No attempt is made here to discuss the nature of the strong (primary) linkages induced by carbon blacks. It was formerly suggested by Blanchard² *et al.* that these were chemisorptive, but this interpretation is not supported by in-

vestigations of the nature and activity of carbon black surfaces by Polley, Schaeffer, and Smith⁷, and more recently by J. W. Watson and Parkinson⁸ (to be published).

Although the concepts of reinforcing action suggested in this paper do not consider the configuration of carbon particles in rubber, they may nevertheless be related to ideas which have been developed concerning the formation of insoluble bound rubber or carbon gel⁹ (Sperberg, Svetlick and Bliss; Sweitzer; Sweitzer, Goodrich and Burgess), for this phenomenon would be influenced by a strong type of linkage. The formation of increased numbers of strong linkages by certain heat treatments leading to improved reinforcement is suggested by recently published researches on Butyl rubber¹⁰ (Gessler; Gessler and Ford). The mechanism or mechanisms of such strong bonds is a problem which remains to be solved.

ABSTRACT

Fillers with little effect on abrasion resistance differ further from carbon blacks in having little or no tendency to introduce some form of strong-type linkage which could stiffen and strengthen the rubber at high extensions. Such linkages are here termed primary to distinguish them from secondary (weak-type) linkages, which have a range of lower strengths as revealed by breakage with applied stress, and contribute little to reinforcement. The abrasion resistance for a given filler concentration is much improved even by remarkably small numbers of primary linkages if the particles are sufficiently small; and it is comparatively insensitive to the number of primary linkages in the quantities normally obtained with carbon blacks. For instance, a considerable degree of reinforcement is obtained with the partially graphitized black known as Graphon, although this black shows drastically reduced capacity to form linkages and little change in particle diameter. The large differences in the wear resistance of vulcanizates containing different grades of carbon black must therefore be attributed mainly to the particle diameter itself rather than to the linkages formed. Moreover, primary linkages as reflected by stress-strain measurements could not explain the effect of particle diameter on reinforcement because they are unrelated to particle diameter. For good wear resistance the particles probably need to have macro-molecular dimensions, though small.

To regard the effect of particle diameter in terms of the interfacial area for linkage formation is inconsistent with the above conclusions. For a given dispersion and concentration of filler it is suggested that reinforcement is most likely to find proper expression in terms of the number of linkages per particle and the number of particles. This is expressed mathematically in a tentative, empirical form of equation designed to fit general conceptions, and to correlate roughly the abrasion resistance with filler particle diameter and with primary linkages as reflected by stress-strain measurements. The equation implies that reinforcement increases with diminishing particle diameter until an optimum is reached, and thereafter decreases to become negligible for particles of molecular dimensions.

ACKNOWLEDGMENT

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RATE OF ADSORPTION OF HIGH POLYMERS ON CARBON BLACK IN RELATION TO THEIR MOLECULAR WEIGHT *

A. I. YURZHENKO AND I. I. MALEEV

IVAN FRANKO LVIV STATE UNIVERSITY, LVIV, U.S.S.R.

The nature and rate of adsorption of high-molecular substances on carbon black is of interest in a number of instances, particularly in the development of adsorption methods of fractionation of high-molecular substances, but also in the use of carbon black as a filler for rubber; the number of papers on the adsorption of high-molecular compounds is small.

The effect of the molecular weight of different polymers on the rate of adsorption of high-molecular substances from their dilute solutions at $C = 0.1-0.25$ per cent was studied in this work. Samples of polyisoprene, polystyrene, emulsion polymerization at a temperature of $+5^\circ$ and $+50^\circ$, and also a plant sample of SKS-30 rubber, were the objects of the investigation. Moreover, a series of polystyrene fractions was obtained by the method of fractional precipitation from methyl ethyl ketone and butyl acetate, using methanol as the precipitant. For all the polymers and their fractions the characteristic viscosity was determined, from which the molecular weight value of the polymer was determined. Carbon black of the Ukhtinsky and Dashavsky factories was used as the adsorbent, the specific surface of which was determined by the adsorption of acetic acid from a benzene solution.

The following relative values of the specific surface of carbon black (in $m^2/g.$) were obtained: special carbon black 220.6; furnace carbon black 89.1; and channel carbon black 10.0.

The adsorption experiments were carried out at $+20^\circ$ in sealed ampoules, with agitation. 0.5 g. of carbon black and 15 ml. of a 0.25 or 0.1 per cent solution of the polymer in benzene were placed in the ampoules. At the end of the experiment the ampoules were opened and the relative viscosity of the centrifuged solution was determined. The special carbon black of the Ukhtinsky factory had the highest adsorption capacity. It completely adsorbed polystyrene, polyisoprene and SKS-30 rubber from solution under the conditions specified. Complete adsorption was not observed for the other carbon black samples, whereby the furnace carbon black, having the smallest specific surface, adsorbed polystyrene to a greater extent than did the channel carbon black. Thus, the specific surface value of the adsorbent in a given case does not determine the adsorption capacity, which depends on the differences in structure and other properties of the carbon black.

The rate of adsorption of a high polymer from solution depends to a considerable extent on the size of its molecules. The lower the molecular weight of the polymer, the greater is its rate of adsorption on a solid adsorbent. This is expressed by the increase of the tangent of the angle of slope of the line tan-

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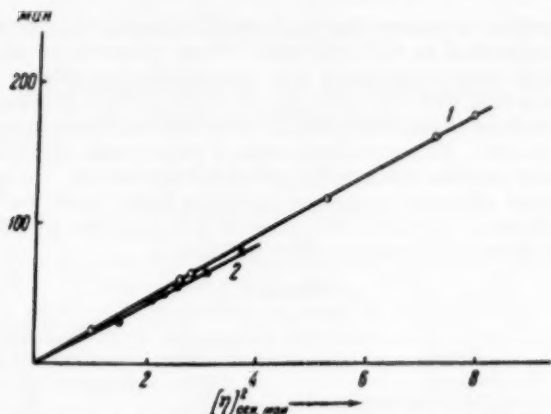


Fig. 1.—Relation of time of complete adsorption of polymer to the square of the intrinsic viscosity. 1—Polystyrene fraction, concentration of original solution, $C = 0.1\%$. 2—Polystyrene, $C = 0.1\%$. The ordinate indicates the time in minutes; the abscissa the square of the molar intrinsic viscosity $[\eta]^2$.

gent to the kinetic adsorption curve (polymer concentration in solution—adsorption time), and also by the decrease of time of complete adsorption with decrease of the molecular weight. The time of complete adsorption was determined as the time necessary for complete disappearance of the polymer from the solution.

It was found that the time of complete adsorption increases linearly with an increase of $[\eta]^2$ of the original polymer, whereupon the same picture was observed for both the non-fractionated polymers, and for their individual fractions. Polystyrene, and also its individual fractions, which have the same intrinsic viscosity, adsorbed at approximately the same rate (see Figure 1). Also the rate of adsorption of polystyrene, obtained at a temperature of $+5^\circ$, differed little from that obtained at $+50^\circ$ (see Figure 2).

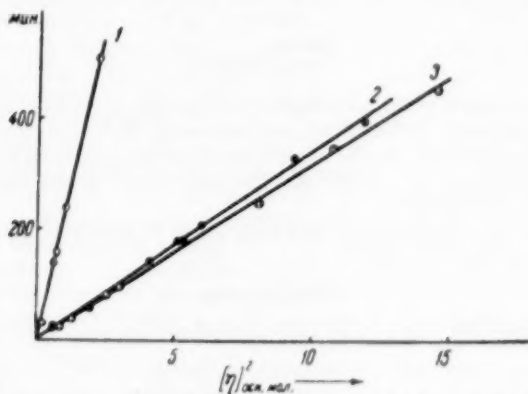


Fig. 2.—Relation of time of complete adsorption of polymer to the square of the intrinsic viscosity. 1—Polyisoprene, $C = 0.1\%$; 2—Polystyrene, obtained at $+5^\circ$, $C = 0.25\%$. 3—Polystyrene, obtained at $+50^\circ$, $C = 0.25\%$. The ordinate indicates the time in minutes; the abscissa the square of the molar intrinsic viscosity $[\eta]^2$.

It is interesting to observe that under stable identical conditions, different polymers are adsorbed at different rates. Thus, polyisoprene was adsorbed on carbon black much more slowly than was polystyrene (Figure 2); the copolymer of butadiene with styrene occupied an intermediate position.

The solvent from which adsorption is carried out has a pronounced effect on the adsorption rate. 0.1 per cent solutions of polystyrene, which had a characteristic molar intrinsic viscosity $[\eta]$ of 46.1 were studied. In general, the time of complete adsorption increases on passing from "poor" to "good" solvents. The times of complete adsorption of a 0.1 per cent solution of polystyrene from different solvents are given in Table 1.

TABLE 1

Solvent	Intrinsic for 0.1% solution	Time for complete adsorption (min.)
Butyl acetate	1.169	15
Methylethyl ketone	1.214	30
Benzene	1.641	40
Toluene	1.530	60
Xylene	1.467	90
Chloroform	2.771	140

In order to determine the specific viscosity of the nonadsorbed portion of the polystyrene, it was separated during the process of adsorption. In the present case, experiments were made in a liter ampoule, into which were placed 26.6 g. of carbon black and 800 ml. of a 0.25 per cent solution of twice-reprecipitated polystyrene. The ampoules were placed in a vibration mixer, and after 20 minutes the contents of the ampoules were centrifuged in a supercentrifuge. The resulting clear solution was evaporated to a smaller volume, after which the polymer was precipitated with methanol. The data obtained are given in Table 2.

TABLE 2

Intrinsic viscosity of original polystyrene sample	Solvent	Intrinsic viscosity of nonadsorbed portion of polystyrene
24	Benzene	45
24	Butyl acetate	60

These data show that for homologous-polymer mixtures, as nonfractionated polystyrene appears to be, small polymer molecules are adsorbed more quickly than are large molecules. In the adsorption of polystyrene from butyl acetate, where the adsorption rate is greater, the enrichment of the high-molecular polymer fractions is greater.

We studied the mechanism of the adsorption of high polymers from their dilute solutions on carbon black.

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MEASUREMENT OF DISPERSION IN BLACK-LOADED RUBBER*

C. H. LEIGH-DUGMORE

DUNLOP RESEARCH CENTRE, BIRMINGHAM, ENGLAND

The reinforcement of rubber by finely divided fillers depends, among other factors, on the smallness of the filler particles. If the reinforcing ability of a filler is to be exploited fully, its particles must be separated from each other in the rubber as completely as possible, i.e., they must be well dispersed. In practice, such perfection is seldom achieved, and aggregates of undispersed particles are to be found.

The adequacy of a dispersion can be assessed by observing directly the numbers of aggregates of different sizes. This can be done with the electron microscope, but the procedure is too unwieldy for regular use.

For most purposes it is sufficient to determine the proportion of the filler which has been dispersed as aggregates smaller than some stated size. This can be done by examining thin sections of the compounded stock under a light microscope.

CUTTING THIN SECTIONS

The best way to prepare sections of rubber thin enough to be examined with visible transmitted light is to cut them while frozen with a sledge microtome; this is the technique of Tidmus and Parkinson¹. Squeeze-out and stretching methods of various kinds have been advocated from time to time, but none is so effective nor so suited for quantitative assessment of dispersion as this microtome method which has been used in Dunlop laboratories for more than twenty years.

The only change that has been made in the original method¹ of sectioning is to substitute glass² for steel knives. Rhomboid-shaped pieces are cut from quarter-inch or 0.375-inch plate glass and the acute-angled edges of about 45° are used for cutting. The two such edges on one "glass knife" will cut as many rubber sections before becoming dull as will a steel knife edge. It is then much simpler and more economical to throw the glass away and cut another piece (from scrap glass from the glazier's shop) than to spend several hours sharpening a steel knife. Razor blades, specially mounted, have also been tried but they leave more knife marks in the section and blade flutter causes uneven thickness. Glass knives leave fewer knife marks than even the best quality steel though when they do appear they are more pronounced.

With experience and reasonable care sections between two and four microns thick can be cut from vulcanized rubber. With greater care sections can be cut thinner still, though not reliably, and thin enough for the electron microscope.

The only way that has been found practicable for removing sections from the knife edge and mounting them for examination involves flooding them with naphtha. This causes swelling and increases the area of a vulcanized rubber section about twice. Vulcanized rubber sections swell uniformly, unvulcanized

* An original contribution. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its meeting in Cleveland, Ohio, May 16-18, 1956.



FIG. 1.—Microtome (with steel knife) and auxiliary apparatus.

ones do not. If the piece of vulcanized rubber which is to be sectioned is measured beforehand (say with the vernier attachment on the microscope stage) and the mounted section is measured again afterwards the amount of swelling can be recorded as the areal swelling factor, s , which is the ratio of these two areas.

ASSESSMENT OF DISPERSION

The sections are examined in a light microscope with a micrometer ruled in squares in the eyepiece, using transmitted light and a total magnification about 70 to 100 \times . The area of agglomerates in the field of view is measured in units of one square of the micrometer by counting the number of squares covered by agglomerates which are each larger than half a square. If the section thickness is small compared with the smallest agglomerates counted, the total area, U , of agglomerates in the field can be taken as proportional to the total volume, V , of agglomerates in the field. So, if the unswollen thickness was t ,

$$V = Ut$$

If $L\%$ by volume of the whole unswollen stock is carbon black, the total volume of black in the field viewed is

$$\frac{Lat}{100}$$

and the proportion of this in the form of agglomerates which have been counted is

$$R = \frac{U}{La} \times 10^4\%$$

If the micrometer has 10^4 squares, and the field they cover had area a unswollen,

$$sa = 10^4$$

where s is the areal swelling factor, and

$$R = \frac{U_s}{L} \%$$

The percentage of the total black content which has been dispersed as agglomerates smaller than those counted is then the dispersion coefficient,

$$\begin{aligned} D &= 100 - R\% \\ &= 100 - \frac{U_s}{L} \% \end{aligned}$$

Once the sectioning technique has been mastered it is not difficult to cut sections regularly 2 or 3 microns thick. Because an areal measurement, U , is used to provide a volume assessment, D , of the dispersion, the smallest agglomerates counted should be larger than the section thickness. In the author's

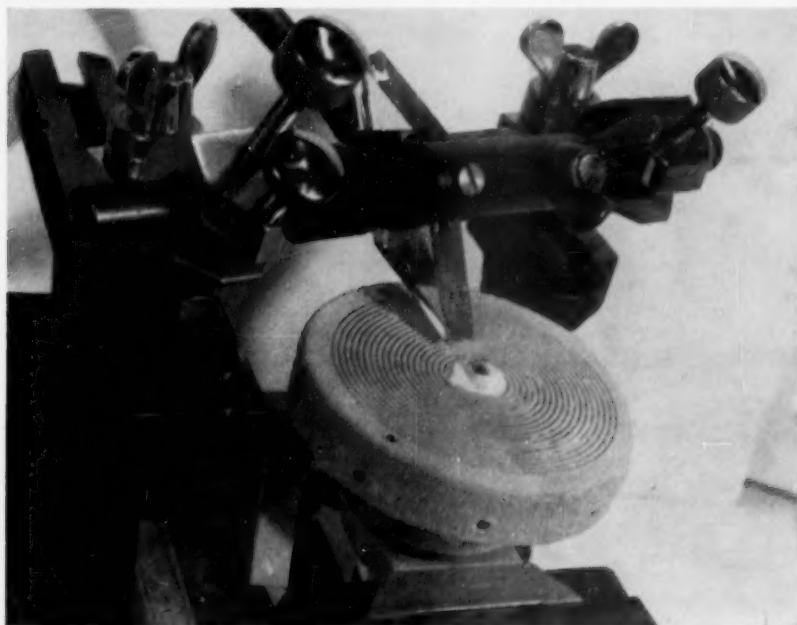


FIG. 2.—Microtome (with glass knife) showing specimen mounted and frozen for sectioning.

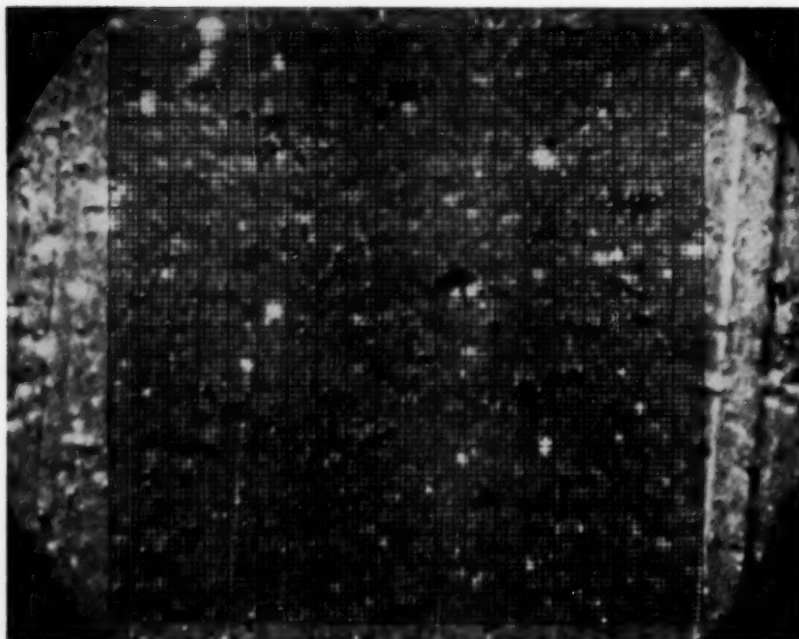


Fig. 3.—Micrograph of rubber section with image of micrometer superimposed.

laboratory the side of a square of the micrometer is equivalent to 13 microns in the plane of the specimen and an agglomerate is counted if its area is half a square or greater.

The method has been found satisfactorily reproducible even between different laboratories. This is demonstrated in Table I.

Measurements of dispersion by this method will readily show up inadequacies of mixing technique. For example, Table II shows dispersion measurements at three stages in the mixing of LTP tread compounds containing HAF and ISAF blacks. Preliminary mixing was little more than sufficient to incorporate the black as powder into the stock. Each stock was remilled twice after intervals of 24 hours. The progressive improvement in dispersion in each case is obvious.

This method of measuring dispersion has also been applied with success to polyethylene-carbon black masterbatches.

TABLE I
REPRODUCIBILITY OF DISPERSION MEASUREMENTS^a IN DIFFERENT LABORATORIES

Specimen	Sectioned in Laboratory X Dispersion measured in		Sectioned and measured in Laboratory Y
	Laboratory X	Laboratory Y	
A	98.5%	98.3%	98.5%
B	93.2%	90.0%	92.7%
C	86.5%	85.9%	85.5%

TABLE II
EFFECT OF MIXING PROCEDURE ON BLACK DISPERSION

Stock	After preliminary mixing	After remilling once	After remilling twice
D	76.8%	90.5%	93.2%
E	51.6%	81.8%	96.1%
F	56.7%	75.2%	85.4%
G	47.8%	78.4%	89.8%

DISCUSSION

It is sometimes argued whether good dispersion is necessarily important since little direct evidence has been collected on the adverse effects of bad dispersion. Little evidence is available, but if, as has been amply demonstrated, particle size and specific surface are critical features of reinforcing fillers it must be necessary to utilize them fully through adequate dispersion.

On the other hand, uniform distribution of the particles may not be essential and is not to be confused with good dispersion. Filler particles may be dispersed, that is separated from each other and each surrounded by rubber, without being uniformly or evenly distributed throughout the mass of the rubber. Electron microscope studies have shown that uniform distribution is probably never achieved and the work of Ladd and Ladd⁵ and of Kruse⁶ suggest that regions or clouds may commonly occur in which there are relatively high concentrations of black though the particles within the clouds may still be well

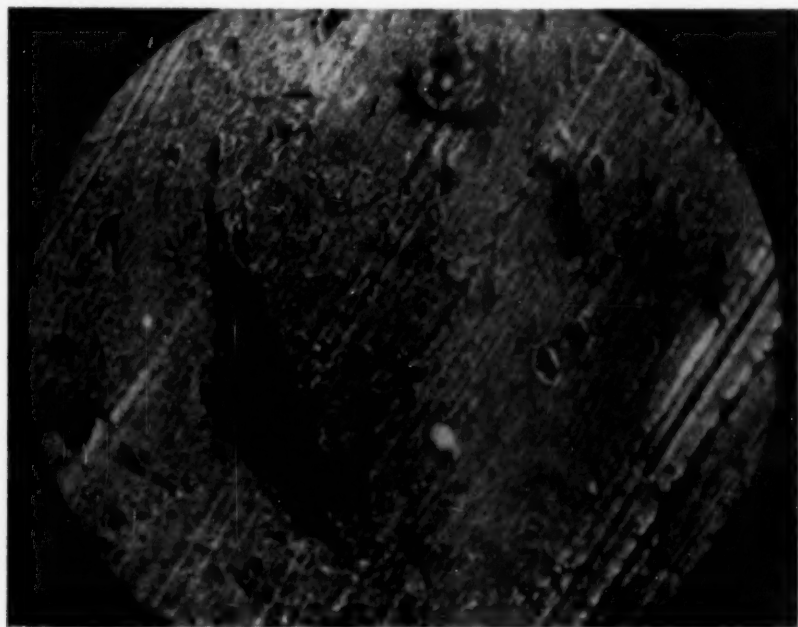


FIG. 4.—Micrograph showing regions of high black concentration.

dispersed or separated from each other. Such non-uniform distribution may or may not be a virtue.

Regions or clouds of this kind can be confused, during light microscope examination of sections, with completely dry aggregates of black, but with experience this becomes less likely. Regions of high black concentration have smoother more regular outlines and are less opaque than aggregates of black alone.

CONCLUSIONS

The gross dispersion of carbon black (or of other particulate fillers) in rubber can be measured quantitatively by cutting thin sections and examining them under the light microscope. The method is very suitable for control of mixing processes either in the factory or the compounding laboratory.

ACKNOWLEDGMENT

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SURFACE TREATMENT OF HYDRATED SILICA PIGMENTS FOR REINFORCEMENT OF RUBBER STOCKS *

R. S. STEARNS AND B. L. JOHNSON

THE FIRESTONE TIRE & RUBBER CO., AKRON, OHIO

Many finely divided solids have been added to elastomers to effect reinforcement of the cured stocks. It is generally agreed that the more finely divided the solid and the greater the degree of physical adhesion (wetting) between the surface of the filler and the polymer chains, the greater will be the general overall reinforcing effect¹. However, recent work on the mechanism of reinforcement has indicated that an important, if not limiting, property of the filler, in at least modulus reinforcement, is the immobilization of polymer segments on the solid surface². The immobilization is effected by the formation of strong chemisorptive bonds, if not covalent bonds, between the polymer and the filler. The application of this concept to carbon blacks has been discussed in detail by the authors, and similar conclusions have been reached by Blanchard and Parkinson³ and by Barton, Smallwood, and Ganzhorn⁴.

Up to the present time carbon blacks are unique as reinforcing agents in Hevea and GR-S type polymers. The numerous inorganic fillers⁵ which have been studied are generally inferior to the carbon blacks in one or more respects. The rubber chemist and technologist is chiefly interested in such properties as modulus, tensile strength, abrasion resistance, and resilience of the compounded stock. Tensile strength and resilience as commonly measured are primarily a function of the extent of surface, the particle-size distribution, and the degree of dispersion of the added pigment or filler. The chemical nature of the solid surface appears to be of secondary importance. Abrasion resistance is a difficult quantity to measure, especially in the laboratory. Therefore, in studying the mechanism of reinforcement and the reinforcing effect of different types of fillers, measurements have been confined to an evaluation of the so-called "equilibrium modulus", from which an apparent work of retraction may be calculated. It has been found that the work of retraction is highly sensitive to changes in the chemical nature of the solid surface and the results may be interpreted in terms of the kinetic theory of elasticity.

In principle, the work of retraction is measured in the following manner². The test-specimen is first conditioned at the highest temperature and the largest deformation to which the sample is to be subjected. The test-specimen is then retracted in small increments, allowing about 45 minutes for stress recovery after each 10 per cent reduction in elongation. The area under the resulting equilibrium stress-strain curve is then measured with a planimeter to give the work of retraction. The limits of integration were kept between 0 and 125 per cent elongation throughout this work and the maximum initial elonga-

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tion was limited to 150 per cent of the unstrained length. The temperature was kept constant at 30° C.

Under the experimental conditions outlined above, the work of retraction as a function of the filler loading may be described by the equation:

$$[W_R]^{1/2} = W_R^0 + \phi v_2 / (1 - v_2)^2 \quad (1)$$

where W_R is the work of retraction of the loaded stock between the indicated limits, W_R^0 is the work of retraction of the gum stock between the same limits, v_2 is the volume fraction of filler present, and ϕ is a constant representative of the reinforcing ability of the filler. ϕ may be considered as a measure of the effect of the filler on the configurational entropy of the polymer chain during deformation as a result of the immobilization of the polymer at the polymer-pigment interface. It has been shown² that:

$$\phi = b(g)^{1/2} \quad (2)$$

where b is a constant, and g is the surface concentration of active sites capable of, and available for, the immobilization of polymer segments. More generally, $g = \sum r_i n_i$, where r_i is the degree of reactivity of a site and n_i is the number of such sites. In applying Equations 1 and 2 to a series of data it is essential that all the curing ingredients and conditions be standardized so that W_R^0 will be constant.

For GR-S stocks containing carbon blacks, it has been shown that the value of ϕ is positive and that furnace blacks have a higher value of ϕ than channel blacks of equivalent particle size. Nonreinforcing pigments, such as Graphon and hydrated silicas, were found to have a value of ϕ equal to zero. According to Equation 2, this means that for these fillers there are no sites on the surface for immobilization of polymer when stress is applied at the polymer filler interface as the result of the gross deformation of the sample.

Inorganic fillers differ from carbon blacks in two respects. First, the essentially spherical carbon black particle is composed of an aggregate of parallel layer groups having a disordered graphitelike laminar structure. Second, carbon blacks contain considerable hydrogen and oxygen, the carbon-hydrogen and hydrogen-oxygen ratios being a distinguishing feature between different types of carbon blacks. It has been suggested that the carbon black particle may be considered as made up of polynuclear benzenoid hydrocarbons of high molecular weight. The surface of such a particle is capable of reacting with oxygen during milling and sulfur during cure to bond the polymer to the black surface through carbon-sulfur-carbon bonds, carbon-oxygen-carbon bonds, or carbon-carbon bonds resulting from free radical type reactions⁶.

If it is assumed that immobilization of polymer segments at the pigment or filler interface is a necessary condition for successful reinforcement, then for stocks containing inorganic fillers the value of ϕ , or the inherent reinforcing ability of the pigment, should be enhanced if the surface of the particle could be treated so as to provide sites whereby the polymer molecule could be immobilized. This immobilization, as a result of the effective increase in the number of cross-linked units in the polymer pigment matrix, would appear as an increase in the modulus of the cured stock.

The experimental work that is described below is an attempt to apply the concepts already outlined to hydrated silica-type pigments. This work was completed in October 1950, before attention was called to the work of Stelling⁷.

TABLE I
COMPOUNDING RECIPE

GR-S 1000	100.0
Sulfur	2.0
Santocure	1.5
ZnO	3.0
Phenyl-2-naphthylamine	0.5
Silica (variable)	6-48
Cured 90 to 120 minutes at 300° F	
Slabs 6 × 6 × 0.075 inch	

The silanes were commercial products, with the exception of two laboratory preparations, the allyl- and the cyclohexenylethyltrichlorosilanes³. The silanes are most easily applied when added to a slurry of the silica in such unreactive solvents as carbon tetrachloride and petroleum ether. However, they may also be applied in the vapor phase or incorporated in the polymer pigment dispersions on a rubber mill or in a Banbury. The unreacted chlorine atoms were removed with methanol. Generally it was found advisable to wash the pigment in dilute alkali to destroy completely all adsorbed hydrochloric acid. Pigment was then dried at 50° C until it reached a constant weight. It is often desirable to add triethanolamine or dipropylene glycol to the stocks, or preferably to the pigment, in order to obtain good cures⁴. In this work when such additives were used, they were adsorbed onto the pigment from a slurry, so that in the cured stocks the pigment-glycol or -amine ratio was a constant as the volume loading of filler increased.

The compounding recipe employed is given in Table I. Because GR-S 1000 does not undergo crystallization on deformation and GR-S has a very flat cure curve, it was chosen as the polymer in which the various fillers were dispersed. In studies of the type undertaken, it is important that the basic compounding recipe not be altered, so that W_R^0 may be considered constant.

The details of the equilibrium modulus measurements have been described². The increase in the work of retraction as filler is added is assumed, on the basis of the kinetic theory, to mean an increase in the number of crosslinked units in the three-dimensional polymer-pigment matrix. The constant ϕ represents the increase in the number of crosslinked units due only to the presence of the filler

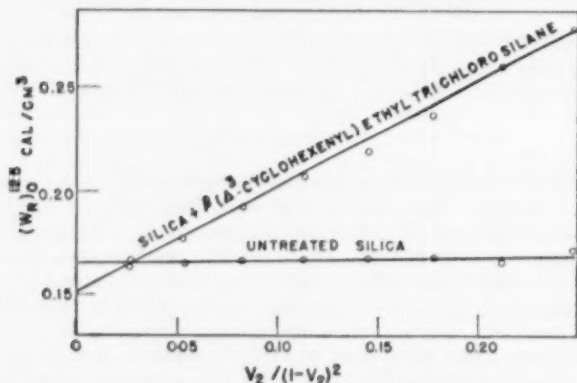


FIG. 2.—Work of retraction as a function of the volume loading of silica.

TABLE II
EFFECT OF SILANES ON MODULUS REINFORCEMENT OF
FINELY DIVIDED SILICA IN GR-S STOCKS

Heat treatment (°C)	Trichlorosilane	Silane (% on silica)	Mole silane/g. silica $\times 10^4$	Additive (%)		$[\phi]_a^{125}$ (cal./cc.)
				Tri-ethanol-amine	Di-propylene glycol	
315	None	—	—	—	—	0.00
120	Vinyl	1	0.62	—	—	0.11
120	Vinyl	1	0.62	—	5	0.18
500	Vinyl	1	0.62	1	3	0.30
500	Vinyl	2	1.24	1	3	0.27
120	Vinyl	5	3.10	—	—	0.00
120	Vinyl	5	3.10	—	5	0.23
None	Vinyl	10	6.20	—	—	0.33
120	Ethyl	10	6.11	—	—	0.10
120	Cyclohexenyl	10	4.28	—	—	0.20
120	Cyclohexyl	10	4.60	—	—	0.00
250	Allyl	15	8.55	—	—	0.36

at a fixed level of cure. The constant ϕ/W_R^0 is to a first approximation independent of the degree of crosslinking in the rubber matrix itself, i.e., the degree of cure of the unloaded gum stock. The constant ϕ is obtained from the slope of the line in plots of the work of retraction $[W_R]^{125}$ as a function of the volume loading of filler, V_2 , as illustrated in Figure 2.

DISCUSSION OF RESULTS

The value of ϕ has been considered as indicative of the inherent modulus-reinforcing ability of a finely divided solid incorporated in a cured rubber matrix. On this basis the increased modulus reinforcement obtained by the introduction of silanes onto a silica surface is shown very clearly in Table II. At low concentration of silanes the presence of triethanolamine and dipropylene glycol is necessary in order to promote the cure. Apparently the amines and glycols serve to reduce the adsorption of accelerator by the silica surface⁶. However, when the concentration of silane is about 10 per cent or greater the silica surface has been sufficiently shielded by hydrocarbon chains to reduce the accelerator adsorption to a point where good cures are obtained.

The change of ϕ as the number of vinyl groups introduced on the silica is increased as shown in Figure 3. The dependence between ϕ and the number of vinyl groups per gram of silane is identical with the dependence found with re-

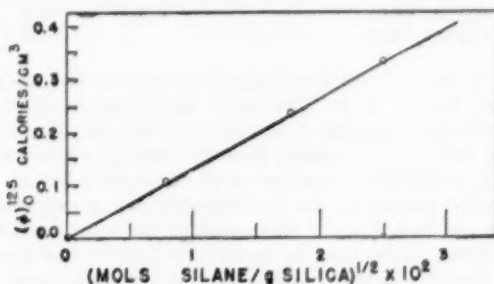


FIG. 3.—Effect of amount of vinylsilane on modulus reinforcement of a finely divided silica.

spect to ϕ and the number of reactive sites on carbon blacks. That silane-treated silicas follow Equation 2 lends support to both the chemical theory of reinforcement and the validity of Equation 2. The results obtained are not dependent on either the heat treatment of the silica previous to introduction of the silane or the presence of either triethanolamine or dipropylene glycol. This is illustrated by the data in Table III.

TABLE III
EFFECT OF HEAT TREATMENT ON MODULUS
REINFORCEMENT OF SILICA IN GR-S STOCKS

Heat treatment (° C)	Dipropylene glycol (%)	Triethanol-amine (%)	$[\phi]_{10}^{100}$, (cal./cc.)
315	—	—	0.00
315	—	6	0.00
315	4	—	0.00
None	—	6	0.08
500	—	5	0.10

The effect of the activity of silica surface on reinforcement was further investigated by variation of the organic radical in the silanes attached to the silica. The activity of five such silanes, added to silica and compounded with GR-S 1000, has been compared by the equilibrium-modulus technique. The molar quantity of silane added is equivalent to 2 per cent of the vinyltrichlorosilane. The relative activity of the silanes is expressed by the figures in the last column of Table IV. The ratio ϕ/W_R^0 takes into account the small variation in W_R^0 which had a value of 0.15 ± 0.03 cal. per cc. for the stocks used. As the data

TABLE IV
EFFECT OF REACTIVITY OF SILANE ON REINFORCING
ABILITY OF TREATED SILICAS

Heat treatment (° C)	Trichlorosilane	Mole silane/ gram silica	Di-propylene glycol, (%)	$[\phi]_{10}^{100}$, (cal./cc.)	$[\phi/W_R^0]^2$
500	$\beta(\Delta^2\text{-cyclohexenylethyl})$	1.25×10^{-4}	5	0.5	12.0
500	Cyclohexyl	1.25×10^{-4}	5	0.39	5.3
500	Ethyl	1.25×10^{-4}	5	0.33	4.4
500	Vinyl	1.25×10^{-4}	5	0.24	2.1
250	Phenyl	1.25×10^{-4}	5	0.24	2.2
500	None	1.25×10^{-4}	5	0.10	0.5
EPC	Carbon black			0.35	5.5
HAF	Carbon black			0.60	16.0

follow Equation 2, at least to a first approximation, and the molar quantity of silane is constant, then it is $(\phi/W_R^0)^2$ which is a relative measure of the immobilization of polymer segments on the silica surface, assuming that the silanes exhibit the same behavior (Equation 2) with respect to ϕ and the number of potential sites for crosslinking reactions as do the carbon blacks.

The effect of the silanes on the modulus-reinforcing properties of silica is evidently due to the fact that the silica surface has been provided with sites, whereby the polymer chains may be immobilized at or near the silica surface predominantly through sulfur bonds. The polymer-pigment dispersion is thereby crosslinked into a continuous three-dimensional matrix. The order

of reactivity observed in Table IV can be explained if it is assumed that the carbon atom adjacent to a silicon atom behaves in a manner similar to a carbon atom adjacent to a double bond, and that the reaction with sulfur proceeds both through an α -methylene hydrogen atom, double bonds, and by ordinary chain transfer. On this basis the β (Δ^3 -cyclohexenyl)ethyl compound has six α -methylene hydrogen atoms, the cyclohexyl compound has one very active hydrogen on a tertiary carbon adjacent to the silica, the ethyl has two α -methylene hydrogens, and the vinyl is reactive through the double bond and the phenyl as a weak chain-transfer agent. On this basis the values in the last column of Table IV are at least of reasonable relative magnitude.

The data presented here support the view that reinforcement does involve immobilization of polymer segments on the surface of the finely divided solids used as reinforcing agents. This immobilization is apparently the result of the crosslinking of the polymer chains to the solid surface predominantly through vulcanization-type reactions. Inactive surfaces such as silicas, clays, and aluminas may by various treatments be converted into active surfaces. This has been accomplished in the case of silicas studied in this paper by reaction of the silica surface with silanes having reactive hydrogen atoms. The degree of modulus reinforcement can be correlated with the activity of the organic silane radical attached to the silica. The modulus-reinforcing ability of silicas treated in this manner compares very favorably with that of the HAF and EPC carbon blacks, as shown by the last two entries in Table IV.

ACKNOWLEDGMENTS

The authors wish to thank F. W. Stavely and members of the Firestone research staff for their interest and assistance; especially L. J. Kitchen for the preparation of the silanes, and The Firestone Tire & Rubber Company for permission to publish this work.

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REACTION OF NATURAL RUBBER WITH HYDROFLUORIC ACID *

D. H. E. TOM

RUBBER-STICHTING, DELFT, HOLLAND

INTRODUCTION

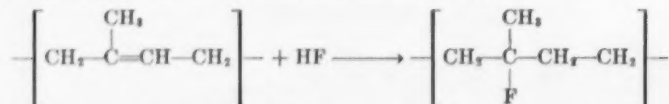
Within the scope of the research on natural-rubber derivatives carried out in the Rubber-Stichting laboratories, attention was also paid to the reaction of rubber with hydrofluoric acid.

Very little work in this field has been achieved by other investigators. The results of their work are mainly to be found in a number of patents¹. These deal with the preparation of products incompletely described that undoubtedly must be considered as more or less completely cyclized rubbers. The fluorine content of these products is, generally speaking, very low and is often said to be lost on heating or storing. According to Nielsen², it would be possible to obtain products with 30 per cent fluorine when using gaseous hydrofluoric acid. This high percentage is tentatively explained by adopting the incorrect formula H_2F_2 for hydrofluoric acid. Elsewhere it is stated either that HF cannot be added to rubber³ or that the addition product is not stable⁴.

METHOD

The reaction of rubber with HF may take place by routes *a* or *b*.

(a) Addition of HF to the double bonds according to:



In this reaction fluorine is added to a theoretical maximum of 21.6 per cent. The progress of this reaction may be observed by fluorine analyses.

(b) Cyclization of the rubber molecule under the influence of HF, similar to the cyclization under the influence of H_2SO_4 and Friedel-Crafts catalysts. This reaction gives rise to a loss of double bonds and to a considerable change of the physical properties. Cyclization can also occur as a consecutive reaction of (a) whereby HF is split off.

The tests have been carried out as follows:

To 5 g. of rubber in 100 cc. of solvent in a bottle of polythene, a mixture of anhydrous HF and dioxane (ratio 1:1) was added. Dioxane served for improving the solubility of HF in the solvent. In all experiments an excess of HF was used (10 g. of HF on 5 g. of rubber). After shaking and keeping the mixture at the reaction temperature desired it was poured into methanol causing the product to coagulate. After reprecipitation from $CHCl_3$ the product was dried in a vacuum. Its F content was determined by melting with potassium and precipitating the fluoride as $PbClF^5$.

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For an estimation of the amount of double bonds not lost by cyclization we used a method adopted by van Veersen³. For this purpose the product was swollen in a mixture of toluene and dioxane and subsequently saturated with HCl. After a 24 hours' reaction at room temperature the chlorine content was determined. All fluorine was now found to be replaced by chlorine. The chlorine content is therefore a measure of the number of unreacted double bonds together with the number of double bonds to which HF had been added. This method is only a rough one, because the addition of HCl to unmodified rubber is effective for not more than 90 per cent.

TABLE I
INFLUENCE OF DURATION AND TEMPERATURE OF THE REACTION

Reaction temp. (° C)	Reaction time (hours)	F content of product (%)	Double bonds saturated with HF (%)	Cl content after HCl addition (%)	Double bonds saturated with HCl (%)
-26	2	15.4	66	28.4	77
	6	16.5	72	28.7	78
	74	16.7	73	26.3	69
-15	1	13.2	55	28.4	77
	5	15.2	65	27.8	75
	19	15.9	68	28.0	76
	100	15.1	64	27.3	72
0	1	15.4	66	26.5	70
	2	16.7	73	24.6	62
	4	13.4	56	24.8	63
20	1/6	11.8	48	28.2	76
	2/3	12.3	51	26.3	69
	1	14.6	62	25.8	67
	2	13.4	56	25.0	64
	5	10.7	43	17.7	41
	22	7.6	30	16.3	37
40	1/2	0	0	13.7	31
	1	0	0	11.5	25
	3	0	0	6.0	7

INFLUENCE OF THE DURATION AND TEMPERATURE OF REACTION

Table I shows the results of a number of tests in which both the duration and the temperature of the reaction are different. Xylene was used as solvent. The percentages of the double bonds being saturated with HF or HCl have been calculated from the fluorine and chlorine content. The last figure thus gives an estimate of the percentage of double bonds not cyclized.

It may be seen from these results that addition and cyclization occur in a competitive way. During the reaction the fluorine content goes through a maximum. The cyclization continues to increase. This may undoubtedly be explained by the fact that HF once added may be split off again (eventually under simultaneous cyclization) whereas the cyclization is irreversible. It is a well-known fact that cyclization proceeds much faster at a high temperature. That is the reason why the maximum of addition occurs at an earlier stage when using high temperatures. The higher the temperature the lower the absolute value of this maximum. At 40° C no addition, but only a fast cyclization occurs.

INFLUENCE OF THE SOLVENT

It is obvious from what precedes that addition plays a more prominent part if the conditions are chosen so as to attain a slow rate of cyclization. This also appears from the influence of the solvent. Van Veersen⁴ has already found that the rate of cyclization decreases in the series: benzene > toluene > xylene, a phenomenon that may be correlated with increasing donor properties, i.e., increasing interaction of these solvent molecules with the catalyst.

Table II shows a number of tests carried out in different solvents. The highest fluorine content is obtained in xylene. In carbon tetrachloride and chloroform no addition, but only cyclization, occurs.

It may, consequently, be concluded that it is possible, by the addition of HF to rubber at lower temperatures and in xylene as solvent, to obtain products of which 65 to 70 per cent of the double bonds are saturated. The HCl addition shows that most of the remaining double bonds have for the greater part disap-

TABLE II
INFLUENCE OF THE SOLVENT

Solvent	Temp. (° C)	Reaction time (hours)	F content of product (%)	Double bonds saturated with HF (%)	Cl content after HCl addition (%)	Double bonds saturated with HCl (%)
Benzene	-15	4	11.2	46	25.3	66
		22	11.1	45	18.8	44
Toluene		4	12.4	51	25.0	64
		22	12.2	50	22.9	57
Xylene		4	15.1	64	28.0	76
		22	15.9	68	28.0	76
Toluene	20	2	4.4	17	13.0	29
Xylene		2	13.4	56	25.0	64

peared by cyclization. We have not been able to attain higher fluorine contents. On carrying out further tests, constant use has been made of this product with a maximum of fluorine content. It is a rubbery material with a specific gravity of 1.04. x-Ray examinations showed a total absence of crystallinity.

EXAMINATION OF THE FLUORINE-CONTAINING PRODUCTS

STABILITY OF THE C-F BONDS

On drying the products of which the preparation was described above, the thermal stability proved to be fairly good. Heating in a vacuum at 100° C for 14 hours did not influence its fluorine content. Only in those cases in which the products had not sufficiently been washed out and still contained traces of HF used for their preparation could a sudden decomposition with simultaneous formation of HF and cyclized rubber occur.

On heating the material in different solvents, in sealed glass tubes, the splitting-off of HF proved to be strongly dependent on the medium, as shown in Table III. 50 mg. of the product containing 16.4 per cent F was heated each time in 2 cc. of solvent and the residual fluorine content was determined after coagulation, washing and drying.

It shows that the stability in an alkaline medium is a very good one. A comparison with hydrochlorinated rubber, which splits off⁷ in aniline at 100° C in one hour half of the HCl, is favorable for the fluorine-containing material.

TABLE III
THERMAL STABILITY OF HF-RUBBER IN VARIOUS SOLVENTS

Medium	Temp. (° C)	Time (hours)	Splitting-off of HF (% of original content)
Dioxane	100	18	6
	130	18	100
Dioxane + 0.5% H ₂ SO ₄	80	4	38
	100	2	66
Aniline	100	17	2
	120	17	20
Benzene	100	18	100
Benzene + 10% aniline	100	17	6
Chloroform	100	18	100

In dioxane the stability is good, too, but the addition of traces of H₂SO₄ leads to a rapid splitting-off. The material is unstable in benzene and chloroform, but improvement is obtained by the addition of aniline.

It is obvious that the HF addition product may be assumed to have a rather good thermal stability, provided that strong acids and free HF in particular are absent.

VULCANIZATION AND MECHANICAL PROPERTIES

Vulcanization of the HF addition product in a normal vulcanization recipe by means of sulfur and accelerators proved to be possible. The addition of MgO to the formulas prevented the splitting-off of HF at curing temperature (142° C).

A compound of 100 parts of the HF addition product with 50 parts carbon black, cured with sulfur and Santocure for 30 minutes at 142° C, showed the mechanical properties given in Table IV (for comparison the properties of a comparable natural rubber compound are listed). It is seen that the material has good mechanical properties, combined with swelling characteristics quite different from those of natural rubber.

In addition, the material has been found to possess the following particular characteristics:

(1) Absolute resistance to ozone at concentrations in which natural rubber and Neoprene decayed.

(2) Low absorption of oxygen. It proved to be 0.056 cc./g./hr. at 100° C and 1 atm. oxygen pressure. A comparable natural rubber compound absorbs 0.18 cc./g./hr.

TABLE IV
MECHANICAL PROPERTIES

Mechanical properties	HF addition product	Same after 4 weeks in air oven at 70° C	Natural rubber
Tensile strength (kg./cm. ²)	230	205	300
Elongation (%)	430	289	550
Modulus at 300% elongation (Kg. cm. ²)	160		90
Hardness (Shore A)	82	90	65
Permanent set after 200%, elongation for 24 hrs. (%)	8		8
Tear resistance (kg./cm. ²)	56		180
Swelling in hexane at 20° C (%)	33	29	260
Swelling in acetone at 20° C (%)	94	65	15

(3) Low permeability to gases. For nitrogen this was found to be 3 per cent of that of natural rubber. Consequently, it is even lower than that of Butyl rubber.

The material has, however, a tendency to become brittle at low temperatures. The brittle point proved to be at -5°C . The resilience showed a minimum at 10°C .

ACKNOWLEDGMENTS

The author wishes to thank Professor M. Stacey (Birmingham University) for hospitality during the early stages of the fluorine research program and the Directors of the Rubber-Stichting for permission for publication. The work described was carried out at the Rubber-Stichting laboratories, in close consultation with G. J. van Amerongen and J. van Alphen, under the management of H. C. J. de Decker.

SYNOPSIS

The reaction of natural rubber with hydrofluoric acid is described. It shows that both addition and cyclization occur in a competitive way. By carrying out the reaction at a low temperature, however, and using xylene as a solvent, cyclization could be forced back to a considerable extent. Products were obtained of which 65 to 70 per cent of the double bonds were saturated with hydrofluoric acid. This addition product has a surprisingly good thermal stability and can be cured to a rubber with good mechanical characteristics, limited swelling power in aliphatic hydrocarbons, absolute resistance to ozone, and small permeability to gases. Its brittle point is rather high.

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THE SORPTION OF WATER BY RUBBER *

D. A. TESTER

BRITISH INSULATED CABLES LTD.,
38 WOOD LAKE, LONDON, ENGLAND

INTRODUCTION

The absorption of water by rubber is a relatively slow process, which may give rise to two different kinds of absorption-time curves: (a) those which proceed to an equilibrium value, or (b) those which appear to show an absorption that increases indefinitely with time.

Numerous attempts have been made, some empirical, others having a theoretical basis, to set up a rate equation relating the quantity of water absorbed to the time taken for the absorption to occur. Absorption isotherms of the nonequilibrium type were found by Boggs and Blake¹ to be best represented by the expression:

$$x = kt^n$$

since the logarithm of absorption usually gives an approximately straight-line relationship with time in these cases.

Andrews and Johnson² derived an expression for the rate of absorption from Fick's law of diffusion:

$$d\theta/dt = D(d^2\theta/dl^2)$$

where θ is the concentration of water at a plane at depth l at right angles to the direction of diffusion, at time t , and D is the diffusion constant.

This expression was integrated to obtain an equation for the concentration of water at a plane after a known time, in terms of the thickness of the slab of rubber. However, this theoretical equation was not generally found to be satisfactory and Daynes³ showed quite clearly that the gas diffusion equation quoted above is quite inapplicable to the case of water absorption by rubber. The absorption seems to be largely due to the formation of a solution of the water-soluble constituents present as a small percentage of natural rubber. Consequently, the diffusion rate will be proportional not to the water concentration in the rubber but to the osmotic pressure gradient between the water, or aqueous solution outside, and the solution formed within the rubber. Daynes therefore proposed in the place of the normal diffusion equation:

$$d\theta/dt = D_1(d^2h/dl^2)$$

where the *equivalent humidity* h is defined as the humidity that would be in equilibrium with the internal solution.

This modified equation may be written as:

$$dh/dt = D_1(dh/d\theta)(d^2\theta/dl^2)$$

Daynes pointed out that $d\theta/dh$ is not constant—as a plot of equilibrium absorption-ambient humidity shows—and therefore the solutions to the gas

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diffusion equation cannot be used to determine h or θ as functions of t , or to obtain the total quantity of water absorbed at a time t , by integration of θ with respect to 1.

No expression has been derived in the literature which is of general application for expressing the course of absorption. Nonequilibrium absorptions are represented fairly well by the power law $x = kt^n$, but such equations are purely empirical and cannot represent an equilibrium type of isotherm. Daynes presented the most exact approach but the differential equation he derived has not yielded a solution.

In this paper, an equation relating water absorption by rubber to time of immersion is derived from a consideration of the osmotic mechanism of the absorption. The equilibrium-type isotherm will be shown to be represented satisfactorily by such an equation, while the characteristics of the nonequilibrium type will be shown to be due in vulcanized rubbers to oxidative aging of the rubber during immersion.

THEORETICAL

The experimental studies of Daynes³, Lowry and Kohman⁴, and others leave no doubt that the absorption of water by rubber consists largely of the formation of a saturated solution of water solubles, followed by the dilution of this solution by osmotic diffusion. In the case of unvulcanized rubber this process would be expected to continue until the vapor pressure of this solution is equal to that in the ambient atmosphere. Thus, absorption by unvulcanized rubber from pure water should proceed indefinitely, producing a nonequilibrium type of curve. In the case of vulcanized rubber, however, the osmotic pressure of the internal solution is opposed by a three-dimensional tension in the rubber, which must swell to accommodate the water, so that an equilibrium-type absorption curve should be obtained. Experiments carried out in the present work have shown that the volume increase is almost exactly equivalent to the volume of water absorbed. It is therefore reasonable to assume that the tension, which is proportional to the volume increase producing it, is thus proportional to the weight of water absorbed. For small extensions, up to about 25 per cent, tension in stretched rubber is directly proportional to extension. Thus we may write:

$$dx/dt = K(\pi - kx) \quad (1)$$

where π = osmotic pressure at time t after immersion, x = weight per cent uptake of water at time t , and K and k are constants.

The value of K is a function of the initial thickness of the test sample and its water permeability, while k is proportional to the modulus of elasticity for small extensions.

It follows from thermodynamic principles that:

$$\pi = (RT/\bar{V}) \ln (p_0/p) \quad (2)$$

where p_0 and p are, respectively, the ambient vapor pressure and the vapor pressure of the internal solution, at temperature T° Abs. while \bar{V} is the partial molar volume of the solvent (in this case water) at temperature T° .

The vapor pressure p refers to a homogeneous solution of the water solubles in the water absorbed although there is, in fact, a concentration gradient within the rubber. However, the internal solution becomes increasingly homogeneous as equilibrium is approached.

The proportion of water-solubles in rubber is small (about 0.2 per cent by weight was found in the vulcanized crepe used in this work) and, furthermore, the molecular weights of these soluble materials (starch, glue, sugars, glycerol, etc.) are high compared with that of water. The internal solution of water solubles, expressed as a mole fraction, is therefore very dilute, except in the initial stages of absorption. Thus, with the usual assumptions for dilute solutions, we may write, for a constant temperature:

$$\pi = k'(n_2/n_1) \quad (3)$$

where n_2 moles of solutes are associated with n_1 moles of water in the internal solution. While n_2 is a constant for a given rubber, depending on the nature and proportion of water-soluble materials contained in it, n_1 is directly proportional to x , the weight per cent uptake of water by the rubber. Thus we may write:

$$\pi = k'(K'/x)$$

and by substitution in (1):

$$dx/dt = K(k'K'/x) - kx$$

Therefore:

$$dt/dx = x/K(k'K' - kx^2)$$

and:

$$t = (-1/2Kk) \ln (K'k' - kx^2) + c$$

When $t = 0$, $x = 0$:

$$c = (\ln K'k')/2kK$$

Therefore:

$$t = \frac{-1}{2kK} \ln \left(1 - \frac{kx^2}{K'k'} \right)$$

and:

$$x^2 = (K'k'/k)(1 - e^{-2Kkt})$$

That is if we let $K'k'/k = K_1$ and $2Kk = K_2$:

$$x^2 = K_1(1 - e^{-K_2t}) \quad (4)$$

The equilibrium absorption value as weight per cent uptake (x at $t = \infty$) = $K_1^{1/2}$. This equilibrium value is of course independent of the thickness of the test sample and the permeability of the rubber, and in accordance with this, K_1 does not contain K , the value of which depends on these factors.

DEPENDENCE OF ABSORPTION EQUILIBRIUM ON RELATIVE HUMIDITY

A quantitative relationship between the saturation absorption of water by rubber at a given temperature and the ambient vapor pressure can be derived from the rate equation postulated above, i.e.:

$$dx/dt = K(\pi - kx)$$

The absorption isotherm approaches equilibrium asymptotically so that when equilibrium is attained $dx/dt = 0$. Therefore:

$$\pi = kx \quad (5)$$

Also:

$$\pi = (RT/\bar{V}) \ln (p_0/p)$$

On the assumption that the internal solution at equilibrium is dilute (true unless absorption is extremely small):

$$p = Pc$$

where P is the vapor pressure of pure water at temperature T , and c is the molar concentration of water in the internal solution.

Thus, by substitution in (5):

$$kx = (RT/\bar{V}) \ln (p_0/Pc)$$

But:

$$c = n_1/(n_1 + n_2)$$

where n_1 moles of water are associated with n_2 moles of solutes in the internal solution.

Thus since n_1 is directly proportional to x , and n_2 is constant for a given rubber:

$$c = x/(x + k_1)$$

Therefore:

$$kx = \frac{RT}{\bar{V}} \ln \left[\frac{p_0(x + k_1)}{Px} \right]$$

and:

$$p_0 = \frac{Px}{x + k_1} \exp \{k\bar{V}x/RT\} \quad (6)$$

By expansion of the exponential term, Equation (6) becomes:

$$p_0 = \frac{Px}{x + k_1} \left[1 + \frac{kx\bar{V}}{RT} + \frac{1}{2} \left(\frac{kx\bar{V}}{RT} \right)^2 + \dots \right]$$

If pressures are calculated in g./sq. cm., RT is of the order of 10^7 , for temperatures of 0–100° C, while \bar{V} for a dilute aqueous solution is approximately 18. The function kx represents the tension in g./sq. cm. opposing swelling when x per cent of water has been absorbed. Measurements of stresses in vulcanized pale crepe for small linear extensions corresponding to the volume increases found in water absorption indicate that k for this rubber has a value of 15–20 depending on the temperature. Thus $k\bar{V}/RT$ must always be of the order of 10^{-6} and may be neglected in the expansion above.

Equation (6) now becomes:

$$p_0 = Px/(x + k_1)$$

which is of the form:

$$p_0 = x/(A + Bx)$$

EXPERIMENTAL

Water absorption experiments were carried out on a vulcanized rubber of the following composition (in parts by weight):

Rubber (pale crepe)	100
Sulfur	3.5
Zinc oxide	6
Stearic acid	0.5
Mercaptobenzothiazole	0.5

The compound was vulcanized at 140° C for 20 minutes in the form of sheets 0.015 inch thick. Test-samples, 3 inches square, were immersed in water at 25° and at 70° C, temperatures being thermostatically controlled to within $\pm 0.5^\circ$ C. The samples were weighed initially, and after suitable periods of immersion, surface moisture being rapidly removed with filter papers. Absorption experiments were carried out, in the presence of air, under an atmosphere of oxygen, and under an atmosphere of nitrogen. In the last case, the test samples were immersed in water that was boiled under reduced pressure to remove dissolved air and, as far as possible, any air occluded in the rubber. The containing vessels were then flushed through for 15-20 minutes with nitrogen containing less than 10 parts per million of oxygen, and sealed.

WATER ABSORPTION BY PREAGED RUBBER

In addition to the experiments with freshly vulcanized rubber, water absorption measurements were made on aged samples. Sheets of rubber were aged at 70° C in an oxygen bomb for four days under a gas pressure of 400 psi. Water absorption values, for immersion under a normal atmosphere at 25 and 70° C were obtained for test samples cut from these aged sheets.

EFFECT OF VAPOR PRESSURE

Aqueous solutions of sodium chloride of known concentrations, and therefore of known vapor pressure, were prepared. Equilibrium absorption values were obtained for rubber samples immersed in these solutions at 25° C. The solutions were kept in stoppered bottles containing very little free space, so that changes in concentration due to vaporization were negligible. The concentrations used, with their corresponding vapor pressures at 25° C, are shown below.

Concn. of aq. soln. as wt. % NaCl	Vapor pressure at 25° C in mm. Hg
0	23.6
1	23.5
2	23.4
10	21.9
25	17.9

RESULTS AND DISCUSSION

Results have been expressed graphically, absorption being expressed as weight of water taken up as a percentage of the dry weight of rubber. Water absorption measurements versus time for a freshly cured rubber immersed in distilled water at 25 and 70° C, are shown in Figures 1 and 2, respectively. Corresponding results for an aged rubber are shown in Figures 3 and 4. Equilibrium water uptake at 25° C, versus vapor pressure of ambient salt solutions is plotted in Figure 5. In the case of salt solutions equilibrium was reached quickly and it was not found necessary to exclude air.

From Figure 1 it will be seen that water is absorbed less quickly under an atmosphere of nitrogen than under air, and most quickly under an atmosphere of oxygen. Also, the isotherm obtained for absorption under nitrogen would appear to be proceeding to an equilibrium value, while that representing water absorption under air has the form of the "nonequilibrium" type of isotherm. Under oxygen, the rate of absorption actually seems to increase after prolonged immersion.

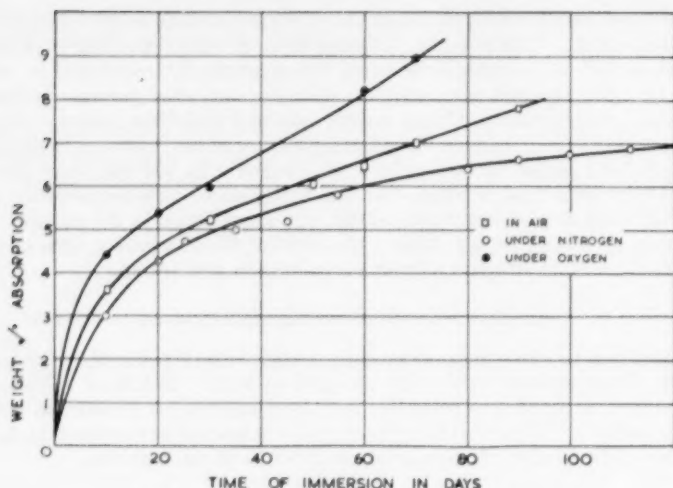


FIG. 1.—Water absorption by vulcanized crepe at 25° C.

From Figure 2, it is evident that an elevation of temperature to 70° C produces a considerable increase in the rate of water absorption under air, and produces a very marked upward inflection in the absorption-time curve. Under nitrogen, the increase in absorption rate is not nearly so marked, especially in the earlier stages.

In Figures 3 and 4, the absorption isotherms for an aged crepe immersed under air at 25 and 70° C, respectively, are compared with the corresponding isotherms for unaged crepe. Aging prior to immersion evidently increased the rate of absorption very considerably, especially at 70° C. Here the characteristic shape of the absorption-time curve is completely changed. After fifty days the aged samples immersed at 70° C had taken up 500 per cent of water and were of a spongelike consistency.

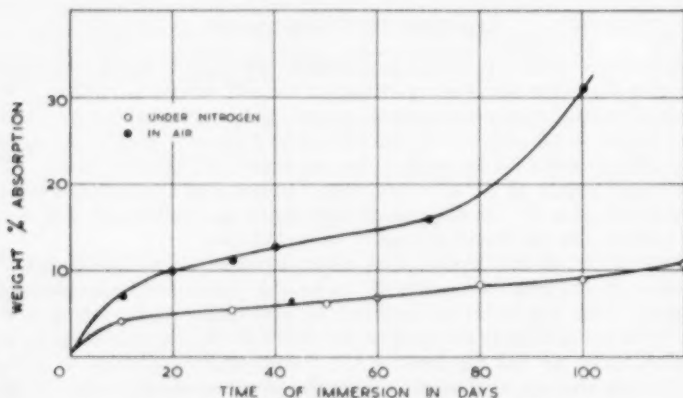


FIG. 2.—Water absorption by vulcanized crepe at 70° C.

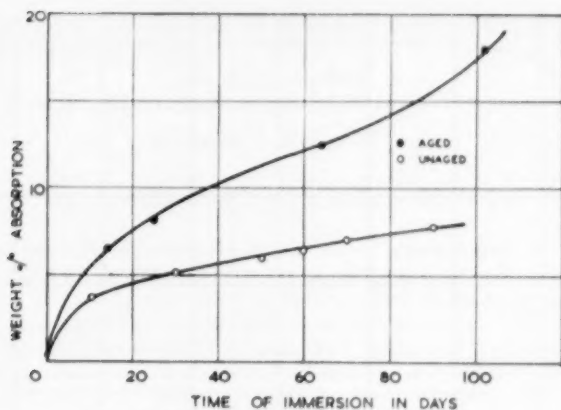


FIG. 3.—Water absorption by aged crepe at 25° C.

It may be concluded from these results that in the absence of oxygen the water absorption-time isotherm for vulcanized natural rubber tends to an equilibrium value and that the rate of absorption does not increase rapidly with increasing temperature. The gradual divergence of the curve at 70° C from the equilibrium type is undoubtedly due to traces of oxygen remaining in the rubber, even after subjection to reduced pressure. For absorption under air at 25° C the water uptake curve diverges only gradually from the equilibrium type, but at 70° C the divergence is very great. The obvious explanation of these phenomena is that, in the presence of air, dissolved oxygen is carried into the rubber by the absorbed water and causes oxidative aging. This brings about a continual relaxation of the stress opposing absorption and prevents the attainment of equilibrium. At 70° C the oxidation and consequently the

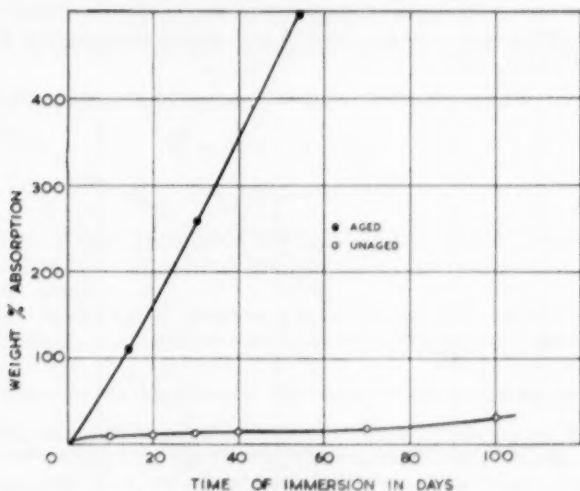


FIG. 4.—Water absorption by aged crepe at 70° C.

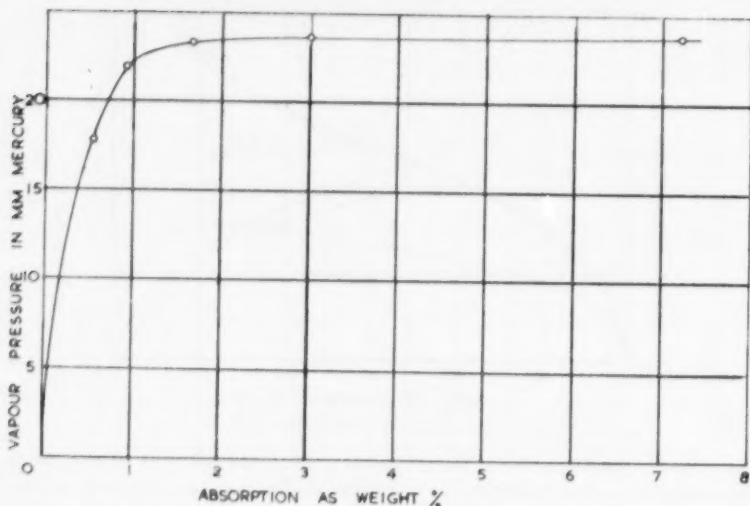


FIG. 5.—Equilibrium water absorption vs. vapor pressure for vulcanized crepe at 25° C.

absorption take place more quickly. Also, since the oxidation is autocatalytic⁵ its effects become increasingly significant and produce an upward inflection of the absorption curve, at 70° C under air, and even at 25° C under oxygen.

These observations are borne out by the water absorption characteristics of rubber previously aged in oxygen. The very marked upward inflection of the absorption-time curve, even at 25° C, indicates an acceleration of further aging by the oxidation products already present.

Absorption-time curves for systems in which oxidative changes are occurring in the rubber cannot be represented exactly by any simple theoretical equation, but the absorption-time equation derived here should be applicable to absorption in the absence of air.

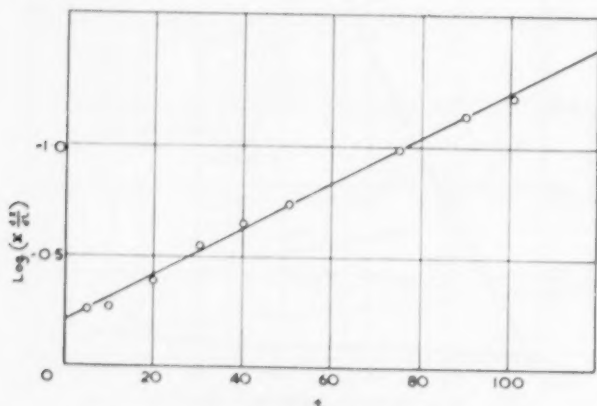


FIG. 6.—Derivation of the constants in $x^2 = K_1(1 - e^{-K_2 t})$.

Its applicability to an experimental curve may be tested and the constants evaluated, as follows: If:

$$x^2 = K_1(1 - e^{-K_2 t})$$

then:

$$2x(dx/dt) = K_1 K_2 e^{-K_2 t}$$

Therefore:

$$\log x(dx/dt) + \log 2 = \log K_1 K_2 - (K_2 t/2.303)$$

Thus a plot of $\log x(dx/dt)$ against t should yield a straight line.

Values of x and dx/dt obtained from the experimental isotherm of absorption under nitrogen (Figure 1) were used to obtain a plot of $\log x(dx/dt)$ against t (Figure 6). A straight-line relationship is in fact obtained. The slope and intercept of this line give values of 52 and 0.023 for K_1 and K_2 , respectively.

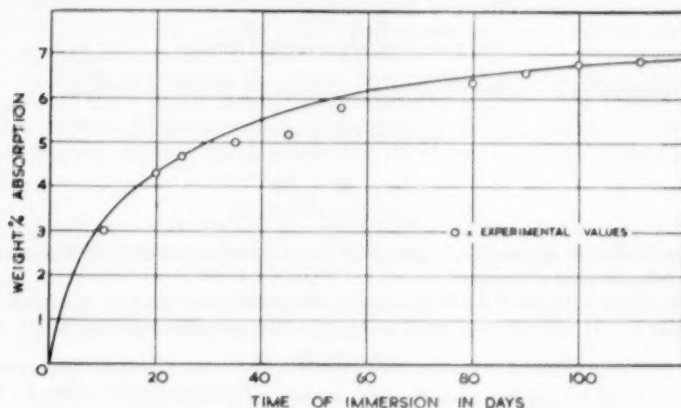


Fig. 7.—Absorption isotherm from the theoretical equation $x^2 = 50.4(1 - e^{-0.023t})$.

The theoretical absorption isotherm at 25° C is thus represented by:

$$x^2 = 52(1 - e^{-0.023t})$$

That is:

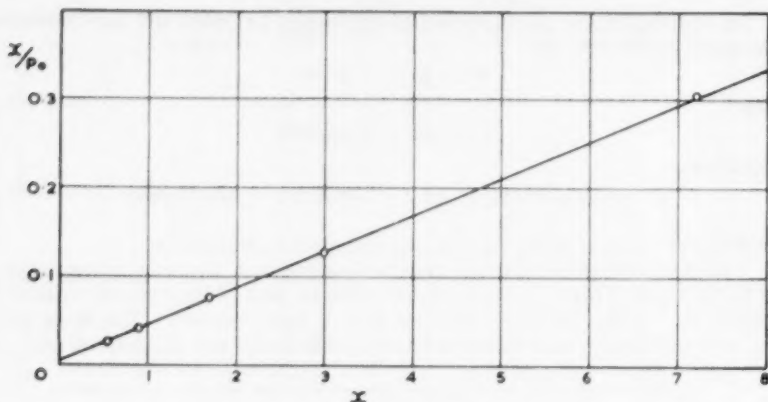
$$x = 7.2(1 - e^{-0.023t})^{1/2}$$

The equilibrium absorption value in weight per cent (at $t = \infty$) is equal to $K_1^{1/2}$, i.e., 7.2 in this case. This value is independent of the surface area or thickness of the test sample.

The theoretical absorption isotherm is shown in Figure 7, together with the experimental values, which will be seen to be in very good agreement with it.

DEPENDENCE OF ABSORPTION EQUILIBRIUM ON VAPOR PRESSURE

The absorption equilibrium value derived above is for absorption from pure water, but, as shown in Figure 5, the equilibrium value is very sensitive to the presence of dissolved salts, because of its dependence on the relative humidity. The equation derived herein correlating water absorption with the ambient

FIG. 8.— x/p_0 vs. x for vulcanized crepe.

vapor pressure at a constant temperature, may be tested as follows: If:

$$p_0 = x/(A + Bx)$$

then:

$$x/p_0 = A + Bx$$

so that a plot of x/p_0 against x should give a straight line. Furthermore its gradient B should equal $1/P$, where P is the saturation pressure of water vapor at the temperature of test.

A plot of x/p_0 against x for the results obtained in the present work is shown in Figure 8. It will be seen that a straight-line relationship does hold. The

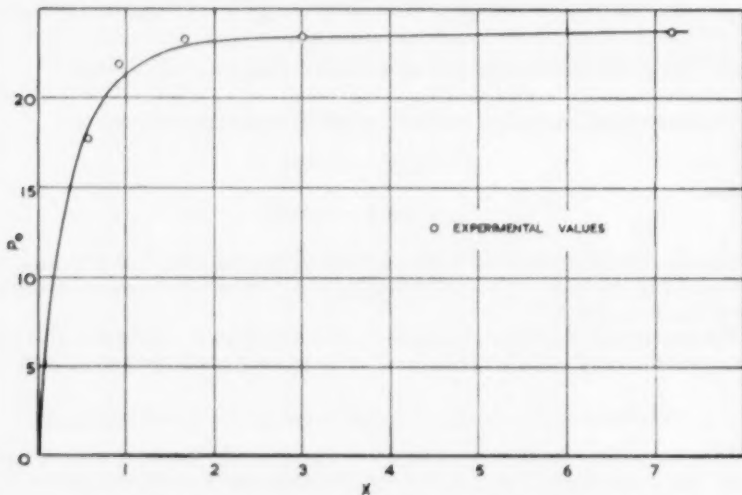


FIG. 9.—Vapor pressure vs. equilibrium water absorption for vulcanized crepe, plotted from the theoretical equation.

constants A and B , obtained from this plot are 0.006 and 0.041, respectively. The function $1/P$ at 25° C equals 0.042. A plot of the relationship:

$$p_0 = x/(0.006 + 0.041x)$$

is shown in Figure 9, together with the values of x against p_0 . There is good agreement between the observed values and the theoretical relationship.

CONCLUSIONS

In the absence of air the absorption of water by a vulcanized crepe rubber tends to an equilibrium value in accordance with an osmotic mechanism of absorption.

An equation for absorption as a function of time, derived by consideration of such a mechanism, represents the experimental data adequately.

A relationship may be derived from the basic rate equation, correlating equilibrium absorption with ambient vapor pressure. This equation also gives good agreement with the experimental data.

The divergence from the theoretical relationship found for absorption in the presence of air may be attributed to oxidative aging of the rubber. This effect is most marked at elevated temperatures, where the results of absorption under nitrogen are very much lower than those for absorption in the presence of air.

ACKNOWLEDGMENTS

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SYNOPSIS

An equation is derived from the consideration of an osmotic mechanism of absorption to represent the absorption-time relationship for a vulcanized rubber immersed in water. The dependence of absorption equilibrium on the relative humidity is also expressed quantitatively. These theoretical relationships are tested for a vulcanized crepe immersed in water and in salt solutions of various concentrations. Good agreement between experiment and theory is obtained for absorption in the absence of air. Divergence from an equilibrium type absorption-time curve in the case in which air is present is shown to be due to aging of the rubber, brought about by oxygen dissolved in the absorbed water. Accelerated aging is shown to be responsible for the marked increase of the rate of absorption brought about by an elevation of temperature, the effect being slight in the absence of air.

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REACTION OF OZONE WITH NATURAL HEVEA AND ACRYLONITRILE-BUTADIENE RUBBERS *

F. H. KENDALL AND J. MANN

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, SHAWBURY, SHREWSBURY,
AND SIR JOHN CANN COLLEGE, LONDON, ENGLAND

INTRODUCTION

The cracking of rubber vulcanizates when exposed to the atmosphere in a state of stress is a well-known phenomenon which has been studied extensively. A comprehensive review of the literature on this subject has been published by Newton¹. Following the lines of earlier work Newton showed conclusively that the cracking is produced by traces of ozone present in the atmosphere. The simultaneous presence of both stress and ozone is required for cracking to occur and the cracks that form are oriented with their lengths perpendicular to the direction of the stress. It has been reported², however, that similar cracking is produced when stretched rubber is exposed to free radicals produced by the thermal breakdown of organic peroxides.

Unstretched vulcanizates do not crack when exposed to ozone, nor do they crack when stretched after exposure to ozone. Apart from the frosting effect described by Tuley³, which is stated to require the presence of moisture and which may require the presence of small stresses, there seems to be no record in the literature of a visible effect being produced by the action of ozone on unstretched vulcanizates. The effect of ozone on unstretched vulcanizates has been investigated more completely and the results are reported in the present paper.

Little is known of the mechanism of the reactions that lead to cracking of vulcanizates and this paper describes experiments designed to throw some light on this. The products of the reaction between ozone and solid rubber have been investigated by means of infrared spectroscopy. Allison and Stanley⁴ have previously described the infrared spectra of products formed from solutions of Hevea and various synthetic rubbers and Salomon and van der Schuer⁵ have recently reported changes which occur in the infrared spectrum of a film of Hevea rubber when exposed to ozonized air.

EXPERIMENTAL

INFRARED MEASUREMENTS

The infrared spectra were measured with a single-beam Grubb-Parsons Spectrometer with rock-salt optics. The air in the spectrometer was dried by circulation through two towers containing activated alumina.

Vulcanizates were measured as films approximately 20 microns thick, obtained by sectioning with a microtome equipped with a freezing stage. Unvulcanized rubbers were examined as films on rock-salt plates. Liquid ozonides were measured in a similar way, while solid ozonides were measured as mulls in Nujol.

* Reprinted from *Journal of Polymer Science*, Vol. 19, Issue No. 93, pages 503-518, March, 1956. The present address of J. Mann is the British Rayon Research Association, Wythenshawe, Manchester.

PRODUCTION AND ESTIMATION OF OZONE

Ozone was produced from air or oxygen by Brodie-type ozonizers; the voltage was applied from a transformer with a continuously variable output. Except where stated in the text, the gases from the ozonizers were passed through caustic soda solution to remove oxides of nitrogen and were then dried by passing over alumina or phosphorus pentoxide.

The ozone concentration was measured by passing the gas through two wash bottles containing potassium iodide solution buffered to pH 6.8. The solution was then acidified and the iodine estimated by titration against 0.1 *N* sodium thiosulfate solution which had been standardized against potassium iodate. The total volume of gas passed through the potassium iodide was measured by a calibrated flow meter.

PREPARATION OF OZONIDES

(a) *α -Cyclohexene ozonide*.—Commercial cyclohexene was purified by fractionation followed by refluxing with maleic anhydride. The maleic anhydride was removed by filtration and the cyclohexene washed successively with water, dilute caustic soda, and water. It was then cooled in a methylated spirit-solid CO₂ mixture, filtered, and dried with quicklime. It was finally passed down a column of activated alumina. The ozonization was carried out at -20° C with oxygen containing approximately 4 per cent by volume of ozone. The method described by Harries⁶ was followed and the final product had a melting point of 72° C.

(b) *1-Methylcyclohexene ozonide*.—1-Methylcyclohexene was prepared from cyclohexanone by a standard method⁷. The purity of the product was checked by comparing its spectrum with the A. P. I. Spectrum No. 897.

The ozonization was carried out in hexane solution at -20° C using oxygen containing approximately 4 per cent by volume of ozone. The hexane was distilled off under vacuum and final traces were removed by pumping at 30° C in a high vacuum. The product was a syrupy liquid.

(c) *Oleic acid ozonide*.—Oleic acid was purified by repeated recrystallization from acetone following the procedure given by Brown and Shinowara⁸. The ozonide was prepared by the method described by Rieche⁹, the final product being a colorless syrupy oil.

(d) *Hevea and gutta-percha ozonides*.—These ozonides were prepared by the method described by Harries¹⁰. Rubber prepared from latex rigorously purified as given below and acetone extracted pale crepe rubber were used, while the gutta-percha was freed from resins by acetone extraction. The final products were very viscous liquids.

(e) *Ozonide from butadiene-acrylonitrile copolymer*.—The copolymer used was the synthetic rubber Hycar OR-15 and the ozonide was prepared by a similar method, using acetone-extracted material.

PURIFICATION OF HEVEA RUBBER

Concentrated centrifuged latex was used as a starting material and all operations were carried out in the dark and under oxygen-free nitrogen. Protein was displaced from the latex particles by sodium oleate followed by repeated creaming in the presence of sodium alginate. The nitrogen content was reduced by this means to 0.02–0.03 per cent.

The resulting latex was dissolved by solubilization in *n*-hexane containing

ammonium oleate and free oleic acid. Part of the rubber was then precipitated by the addition of acetone and the flocculent precipitate so obtained was then extracted with hot acetone to remove oleate soaps and other nonhydrocarbon impurities. The rubber was finally dried in nitrogen at reduced pressure.

PREPARATION OF VULCANIZATES

The vulcanizate used in the infrared work and the work on the effect of ozone on unstretched vulcanizates had the following composition: pale crepe 100, colloidal zinc oxide 0.5, stearic acid 0.5, zinc dibutyldithiocarbamate 0.5, sulfur 2. The mix was cured to give optimum tensile strength and for the work on unstretched vulcanizates thin transparent sheets were molded.

The base mix used in the tests of the effect of antioxidants on ozone cracking was pale crepe 100, zinc oxide 5.0, stearic acid 1.0, cyclohexylbenzothiazyl sulfenamide (CBS) 0.5, sulfur 2.5. Vulcanizates containing one part of the following antioxidants were investigated:

- BLE (acetone-diphenylamine reaction product)
- Thermoflex (di-*p*-methoxydiphenylamine)
- Flectol H (acetone-aniline reaction product)
- Betanox (acetone-phenyl-2-naphthylamine reaction product)
- Santoflex B (acetone-*p*-aminodiphenyl reaction product)
- Agerite Resin D (polymerized trimethyldihydroquinoline)
- Agerite White (*N,N'*-di-2-naphthyl-*p*-phenylenediamine)
- Phenyl-2-naphthylamine
- Antioxidant 4010 (phenylcyclohexyl-*p*-phenylenediamine)

A second series of vulcanizates containing carbon black and one part of the same antioxidants was also investigated, the composition of the base mix being: smoked sheet 100, HAF black 0.50, pine tar 5.0, zinc oxide 5.0, stearic acid 2.5, CBS 0.5, sulfur 2.5.

The tests on these vulcanizates were carried out in the way described by Best and Moakes¹¹ using a Crabtree-Kemp type of exposure chamber and grading the samples visually.

HYCAR MONOLAYERS

The experiments on Hycar monolayers were carried out on a trough similar to that described by Alexander¹². Since the amount of material on the trough was very small, many hundreds of films would have had to be ozonized to obtain sufficient product for an infrared measurement. A method was perfected, therefore, in which the unimolecular film could be spread continuously, thus enabling the reaction product to be collected continuously. A sketch of the apparatus used for this purpose is shown in Figure 1. The Hycar film was spread by allowing drops of 0.02 per cent solution by weight in a 50 benzene-25 acetone-25 chloroform mixture to fall on the water in the trough. The monolayer was blown down the trough by means of a wide jet of ozonized air which had not been passed through caustic soda solution. The product of reaction was picked up on a stainless-steel roller driven by an electric motor and was removed from the roller by a sharp knife edge.

When sufficient product had been collected it was removed and dried by pumping in a high vacuum. A little chloroform was added to the dried product and the resulting gluey mass was spread on a rock-salt plate and the chloroform removed in a high vacuum.

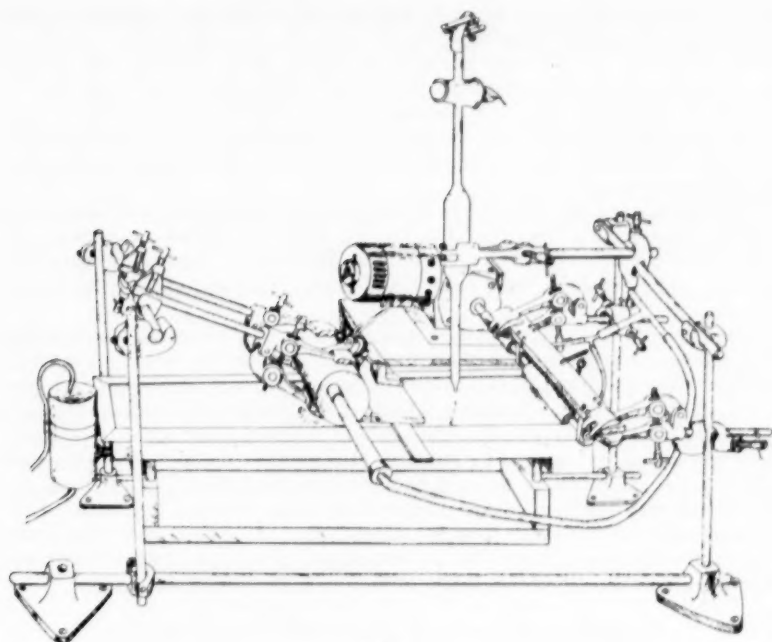


FIG. 1.

RESULTS

EFFECT OF OZONE ON UNSTRAINED VULCANIZATES

When thin films of the pure gum vulcanizate were heated to 70° C for 20 minutes and then exposed to ozonized air (0.01 per cent by volume of ozone) which had been preheated to 70° C they rapidly clouded over and became translucent. Microscopic examination showed the presence of a white film on the surface, which gradually broke up to form filaments of white material when exposed to further ozone. The white filaments could not be removed and seemed to be firmly anchored to the underlying rubber. No change was observed when a film was exposed to unozonized air.

This experiment was repeated over a wide range of temperatures and the time required for the surface to cloud was recorded at each temperature. The results are shown in Table I. The significance of these results is not clear but the figures indicate a very definite change between 40 and 35° C. The reasons for the appearance of cloudiness are complex and probably involve physical as well as chemical processes. However, the figures show why many workers have been unable to observe any change in unstretched vulcanizates at room tem-

TABLE I

Temp. (° C)	Time (sec.)	Temp. (° C)	Time (sec.)
100	<15	40	60
70	<15	35	450
60	15	30	900
50	30		

perature since the time required is so long and when films were exposed at room temperature for periods ranging up to 60 hours the clouding of the surface was easily observed. In this case it might be argued that clouding was brought about by the presence of residual surface stresses in the films, but as it seems very unlikely that such stresses were present in the experiments at elevated temperatures the explanation loses its validity. The experiments are thought to show, therefore, that ozone reacts with unstrained vulcanizates to cause a change in physical appearance.

The surface change observed in the above experiments is reminiscent of the frosting phenomenon described by Tuley³, which is stated to require the presence of moisture as well as ozone. With this in mind the experiments were repeated using carefully dried rubber and ozone; clouding of the surface was still observed.

Experiments have been carried out at room and elevated temperatures using ozonized oxygen instead of ozonized air. No clouding was observed with ozonized oxygen, although one or two unoriented cracks appeared after prolonged exposure. It will be shown later that the reaction between air ozonized by an electrical discharge and natural rubber involves gases other than ozone, gases which may be removed by bubbling the ozonized air through caustic soda solution, and are therefore thought to be oxides of nitrogen. Clouding of the surface still occurred with ozonized air treated in this way and the results of the experiments described above were not altered, suggesting that, under the conditions of the experiment, the oxides of nitrogen are regenerated from the nitrogen after the removal of those originally formed in the electrical discharge.

EFFECT OF OZONE ON UNVULCANIZED RUBBER

The attack of ozonized air or oxygen on unstretched unvulcanized natural rubber was demonstrated with films of purified rubber and pale crepe approximately 200 A. thick. These films were cast from solution onto mercury. When they were exposed to oxygen or air containing approximately 0.01 per cent ozone they lost their rubberlike properties rapidly. The films lost their cohesion and could be broken up into separate islands by using a probe. Frequently the films broke up, seemingly spontaneously, there being a sudden expansion in area with the formation of a multitude of small islands of film.

Owing to the high reactivity of ozone toward rubber, the reaction would be expected to take place initially near the surface and extend into the bulk of the rubber only gradually, when the outer layers have reacted completely. This diffusion control was demonstrated with thin films cast on mercury. Films approximately 200 A. thick lost their rubberlike properties in a few seconds when exposed to 0.01 per cent ozone. This time increased with increasing thickness and films one micron thick retained their rubberlike properties for hours.

INFRARED SPECTRA

When a film of the pure gum vulcanizate approximately 40 microns thick was exposed to oxygen containing 0.01 per cent ozone, the reaction was found to be very slow. After 60 hours' exposure the infrared spectrum of the film had changed only slightly. The presence of carbonyl groups was indicated, however, by a weak band at 1720 cm^{-1} , while a control film exposed to unozone oxygen for the same period showed no change in spectrum.

However, using oxygen containing 0.4 per cent ozone a film of the vulcanizate showed a marked change in spectrum after 3 hours' exposure. There was a

broad band near 3000 cm^{-1} due to hydrogen-bonded OH groups, a band near 1720 cm^{-1} due to carbonyl groups, a band near 1170 cm^{-1} , and absorption in the region of 1020 cm^{-1} had increased.

All these features appear in the spectrum of a natural rubber vulcanizate aged thermally or in light in oxygen free from ozone¹³. The spectrum of the film was in fact indistinguishable from that of a vulcanizate in the early stages of such an oxidation.

The experiment was repeated using the same vulcanizate and a film of a similar vulcanizate containing 1 per cent phenyl-2-naphthylamine. After 3 hours' exposure the film containing no antioxidant showed the changes detailed above while the spectrum of the film containing antioxidant had undergone only a slight change, there being a weak band due to carbonyl groups at 1720 cm^{-1} . The thermal oxidation of natural-rubber vulcanizates in ozone-free oxygen is similarly inhibited by phenyl-2-naphthylamine¹³.

The spectrum of rubber ozonide prepared in solution is shown in Figure 2. This product shows bands at 3300 cm^{-1} due to OH groups, 1720 cm^{-1} due to carbonyl groups, and 1170 cm^{-1} . Although the rubber ozonide showed three bands which appear in the spectrum of oxidized rubber, the two materials can be readily distinguished. Oxidized rubber shows a broad unresolved absorption between about 1150 and 1000 cm^{-1} , whereas the ozonide shows several well-

TABLE II

1-Methylcyclohexene ozonide	1101 and 1070 cm^{-1}
α -Cyclohexene ozonide	1110
Oleic acid ozonide	1091
Hycar OR-15 ozonide	1110
Hevea ozonide	1110 and 1084
Gutta-percha ozonide	1110 and 1084

resolved bands in this region. In particular, rubber ozonide shows two strong bands at 1110 and 1084 cm^{-1} , which can be used to identify its presence in the reaction products. The origin of these two bands is not clear, but since several ozonides that have been prepared show strong bands in this region it would seem that at least one of the bands is caused by a common structural feature in the products. The frequencies of these bands are listed in Table II.

Although the strong bands of Hevea ozonide at 1110 and 1084 cm^{-1} can be used to detect its formation, inspection of the spectrum of Hevea shown in Figure 2 shows that these bands would be masked by a strong absorption of the rubber in the early stages of reaction. This is the reason why the bands were not detected in the vulcanizates described above.

Figure 2 shows the spectrum of a film of purified unvulcanized rubber after exposure to oxygen containing 0.4 per cent ozone for 56 hours. It is evident that an advanced state of reaction had been reached, since the band at 840 cm^{-1} due to the $-\text{C}(\text{CH}_3)=\text{CH}-$ groups has weakened considerably. The spectrum of the product is very similar to that of the ozonide found in solution and in particular showed the strong bands at 1110 and 1084 cm^{-1} . The spectra of the two products are not identical, however. In the spectrum of the product from solution the 1170 cm^{-1} is a shoulder on the side of the much stronger band at 1110 cm^{-1} , whereas in the spectrum of the product from solid rubber the 1170 cm^{-1} was stronger than that at 1110 cm^{-1} . The nature of the chemical grouping responsible for the 1170 cm^{-1} band is uncertain, but it is worth noting that a band at this frequency appears during the oxidations of natural rubber and GR-S¹³, polybutadiene¹⁴, acrylonitrile-butadiene copolymers, and polythene¹⁵.

The difference between these two spectra is not very convincing, however, particularly in relation to the reactions leading to cracking of vulcanizates. The speed of cracking is so great that the reactions involved must take place in a very thin layer at the surface. With the film of unvulcanized rubber, however, a bulk reaction was studied and the product formed initially near the surface was subjected to prolonged action by further ozone as it diffused into the bulk of the rubber. Experiments were therefore carried out with much thinner films of rubber. This enabled the period of exposure to ozone to be reduced considerably so that the initial product of reaction was left in contact with ozone for a much shorter period.

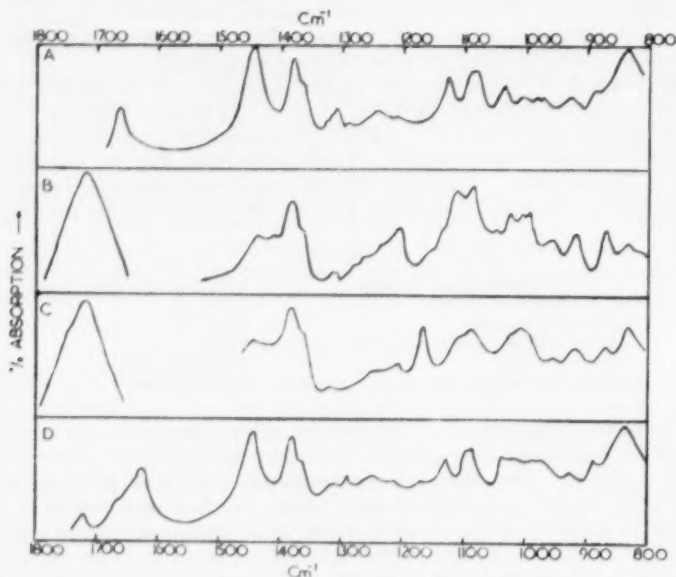


FIG. 2.—(A) Purified natural rubber. (B) Natural-rubber ozonide. (C) Product from thick film of purified rubber and ozonized oxygen. (D) Product from ozonized air and purified rubber.

Films of purified rubber approximately 200 Å. thick were cast from chloroform solution on to the bottom of a large porcelain dish and were then exposed to oxygen containing 0.1 per cent ozone for 30 seconds. The product was removed from the dish by dissolving in chloroform and the chloroform was evaporated under a water pump vacuum, leaving a sticky residue. This was smeared on a rock-salt plate and the final traces of chloroform were removed by pumping in a high vacuum. The spectrum of the product was similar to that of the thicker film with the exception that the 1170 cm^{-1} was weaker, though it was still much stronger than the 1170 cm^{-1} band of the ozonide prepared in solution.

This result on thin films suggests that part of the intensity of the 1170 cm^{-1} band might arise from the further action of ozone on an initial product. A film of the ozonide prepared in solution was therefore exposed to further ozone. Although the band at 1170 cm^{-1} increased in intensity, it was still weaker than the band of the product obtained from solid rubber at room temperature.

EXPERIMENTS WITH OZONIZED AIR

Vulcanized and unvulcanized films have also been studied spectroscopically after exposure to air ozonized by an electrical discharge. After exposure to air containing approximately 0.1 per cent ozone for 7 hours a marked change in spectrum had occurred. The bands observed after exposure to ozonized oxygen were present but the most marked change was the appearance of a strong band at 1624 cm^{-1} . The 1624 cm^{-1} band was much stronger than the carbonyl band at 1720 cm^{-1} and there was a weaker band at 1290 cm^{-1} that did not appear with ozonized oxygen. These bands are shown in Figure 2.

The 1624 and 1290 cm^{-1} bands did not appear, however, when the ozonized air was passed through caustic soda solution and then dried with activated alumina. This shows that the bands were produced by a gas other than ozone. Rowen and Plyler¹⁶ observed bands at 1647 and 1280 cm^{-1} in cellulose which had been reacted with NO_2 and showed that the bands were due to nitrate groups. It seems certain, therefore, that the bands observed in the present work were due to similar groups, presumably formed by the reaction of NO_2 with alcoholic OH groups produced by the ozone. This conclusion is in agreement with the observation that the appearance of the bands is inhibited in vulcanizates containing 1 per cent phenyl-2-naphthylamine.

EXPERIMENTS ON HYCAR OR-15

With HyCar OR-15 it was possible to study the reaction of ozone at the surface in the absence of a bulk reaction by using a monolayer spread on water. The progress of the reaction was followed by surface area-pressure measurements. After a few seconds' reaction with ozone the films became less compressible, the surface area-pressure curve having a steeper inclination. Further reaction with ozone led to a further gradual decrease of compressibility and after prolonged exposure the film seemed to disappear, since no pressure on the barrier was recorded on compressing the film. It is presumed that at this stage the material had passed into solution in the water substrate.

The possibility that hydrolysis of ozonide by the water substrate would vitiate the results has been investigated. A film that had been reacted with ozone was allowed to stand for 0.5 hour and no change in its surface area-pressure characteristics could be detected. HyCar ozonide prepared in solution was also allowed to stand in water and no change in its spectrum was observed. These experiments seem to show that hydrolysis of the product of ozonization is slow under the conditions used.

In order to collect sufficient product for infrared measurements the continuous method of producing films described in the experimental section was used. The spectrum of the product is shown in Figure 3. The product contained unreacted double bonds as was shown by a medium intensity band near 965 cm^{-1} due to $-\text{CH}=\text{CH}-$ groups. Unfortunately it was found that, if the monolayer was ozonized further, it was impossible to remove the product from the trough. The spectrum of the product showed that it was very similar to the product of ozonization as formed in solution at low temperature. In particular it showed bands due to OH and carbonyl groups in addition to a band at 1110 cm^{-1} . A band was also present at 1170 cm^{-1} , though this was weak compared to the band at 1110 cm^{-1} .

For purposes of comparison, a thick film of HyCar OR-15 was exposed to oxygen containing 0.5 per cent ozone for 36 hours. The spectrum of the prod-

uct was similar to that from the monolayer, but differed in that the 1170 cm^{-1} band was more prominent. It seems probable, therefore, that as with natural rubber part, at least, of the intensity of the 1170 cm^{-1} band is due to the further action of ozone on an initial product of reaction.

EFFECTS OF ANTIOXIDANTS ON OZONE CRACKING

In view of the effect of phenyl-2-naphthylamine detected spectroscopically and of the protection afforded by antioxidants to Neoprene vulcanizates¹⁷, the effect of antioxidants on the cracking of natural-rubber vulcanizates was investigated. The compositions of the vulcanizates and details of the test procedure are given in the experimental section.

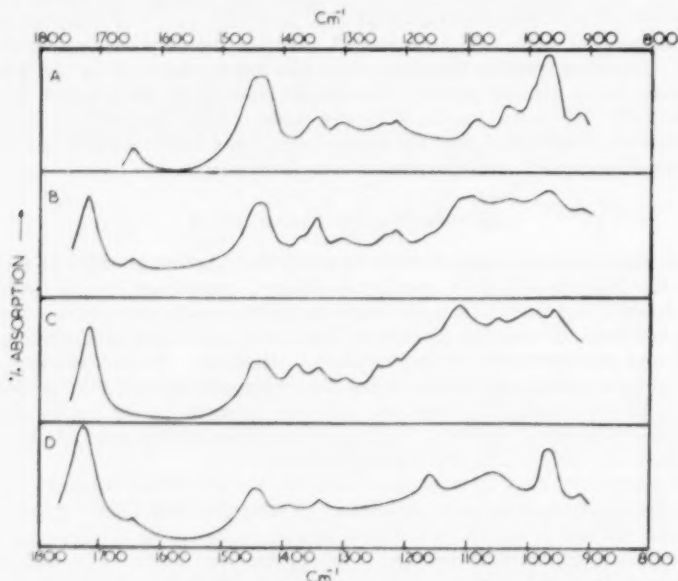


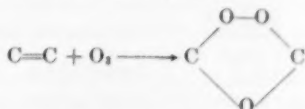
FIG. 3.—(A) Hycar OR-15. (B) Ozonized monolayer. (C) Hycar OR-15 ozonide. (D) Hycar OR-15 oxidized in light.

None of the antioxidants tested provided protection against ozone, though some appeared to have a slight influence on the rate and nature of cracking. The nature of the test is such however that slight differences between vulcanizates are of doubtful significance.

DISCUSSION

The infrared results show that the product of the dark reaction between ozone and solid natural rubber at room temperature is similar to the well-known product formed in solution at low temperature. The latter product is the ozonide of natural rubber which has been known for many years¹⁰. The evidence for the structure of this ozonide came from elemental analysis and its reactions, e.g., products formed on hydrolysis¹⁸. This evidence indicated that the product was an ozonide analogous to the ozonides formed by simple olefins,

whose structure has been investigated by Rieche¹⁹. In the case of 2-butene Rieche succeeded in synthesizing the ozonide and as a result of this work the following structure was established for ozonides:



Criegee²⁰ has shown by synthesis that the monomeric ozonide of 1,2-dimethylcyclopentene has a similar structure.

It has long been clear, however, that the reaction of ozone with carbon-carbon double bonds does not always give a simple product of this type. Thus Rieche¹⁹ and earlier workers have shown that the nature of the product sometimes depends on the solvent medium in which the reaction is carried out.

The product obtained from natural rubber in the present work clearly had a more complex structure than the one given above, since it contained O—H and carbonyl groups. The products obtained from Hycar and the simpler olefins investigated in the present work showed similar features.

Recently Criegee et al.²¹ have shown that some compounds which had been thought to have the ozonide structure given above are not in fact ozonides. The "ozonide" of 9,10-octalin may be cited as an example. The substance formed in the reaction between this compound and ozone has the structure shown below:



The formation of this ketone diperoxide is presumed to take place via an intermediate that splits at the carbon-carbon double bond, giving ions or radicals which then dimerize to form the final product. A similar process occurs in ozonization of tetramethylethylene, when a good yield of dimeric acetone peroxide was formed²¹.

The products identified by Criegee are similar to the benzophenone diperoxide found by Marvel²² in the ozonization of 1,1-diphenyl 1-alkenes. In this work great care was taken to exclude water and it was found that the diperoxide was formed in the complete absence of water with an unchanged yield.

The work of Criegee and Marvel shows that scission at the carbon-carbon double bond frequently occurs spontaneously during ozonization and confirms an earlier suggestion of this kind made by Briner²³.

The infrared and Raman results of Briner²⁴ on the ozonization of simple compounds shows that scission of carbon-carbon double bonds occurs at an early stage in the reaction. In the early stages of reaction Briner observed bands in the range 1780–1680 cm^{-1} , which he attributed to ozonides. It seems more probable that these bands are due to carbonyl groups in scission products.

Table III gives the frequencies observed by Briner and the frequencies of the expected scission products. The frequencies of the first three compounds were measured using 0.025 *M* solutions in carbon tetrachloride. The remaining compounds were not available and the frequencies given (marked asterisk) are those to be expected from the correlations given by Bellamy²⁵.

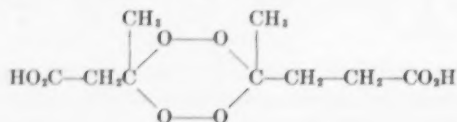
This table makes it clear that the bands observed by Briner are due in four cases to scission products containing carbonyl groups and not to ozonide groups.

TABLE III

Compound	Frequency observed by Briner and attributed to ozonide	Ozone scission product	Frequency of pure scission product
Stilbene	1709	Benzaldehyde	1697 (liquid)-
Styrene	1708		1700 (soln.)
Anethole	1700	Anisaldehyde	1685 (liquid)-
			1691 (soln.)
Methylisoeugenol	1687	Veratric aldehyde	1664 (solid)-
			1694 (soln.)
Cyclohexene	1732	Open-chain aldehyde	1735*
Limonene caryophyllene	1719	Aliphatic ketone or aldehyde groups	1720* or 1735*
	1718		
Nopinene	1718	Nopinone	1720*-1706*
Ethyl maleate	1765	Ethyl glyoxalate	> 1735*

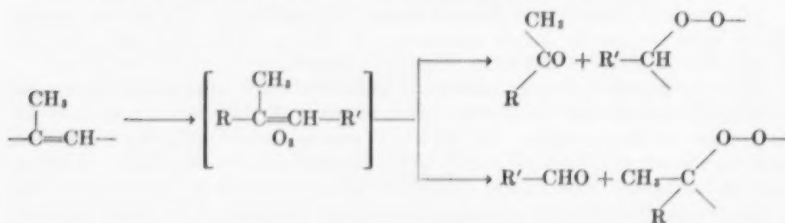
The only case in which the frequency observed by Briner does not agree with the frequency of the expected scission product is methylisoeugenol. Here the ozonization was carried to an advanced stage (50 per cent) and, in view of the ease with which veratric aldehyde is oxidized, the absence of a band due to this product is perhaps not surprising.

The evidence outlined above shows that spontaneous scission at the carbon-carbon double bond is a widespread phenomenon in ozonization. It seems likely therefore that a similar scission occurs during ozonization of rubber. This suggestion is supported by the isolation of levulinic acid diperoxide from the ozonization of natural rubber in solution:



This compound was first isolated by Pummerer²⁶ who found that it was deposited when a solution of the ozonization product was let stand in a stoppered vessel. This substance was occasionally deposited during the ozonization in the present work.

With natural rubber the scission can occur in two ways:



The nature of the final products would depend on the further reactions of the biradicals, but some dimerization to diperoxides could be expected. A scission of this type would account for the presence of carbonyl groups in the product, but the way in which hydroxyl groups are formed is not clear. The experiments with ozonized air suggest that these hydroxyl groups are alcoholic, so that the

OH absorption cannot be attributed to carboxyl groups produced by the oxidation of aldehydes.

The inhibition of the introduction of OH groups by 1 per cent phenyl-2-naphthylamine suggests that they may be formed by a free-radical chain reaction. There are at least two possibilities for such a chain reaction: (a) the scission at the carbon-carbon double bond is itself a chain reaction and (b) the radicals produced by the scission start an oxidative chain reaction involving molecular oxygen by abstraction of α -methylenic hydrogen. This latter possibility would explain not only the formation of alcoholic OH groups, but also the decrease in the intensity of the CH_2 group band at 1460 cm^{-1} relative to that of the CH_3 group band at 1375 cm^{-1} .

This feature, which has also been observed by Salomon and van der Schee⁶, is also characteristic of the thermal and photochemical oxidations of natural rubber where oxidative chain reactions are known to occur. However, these workers argue that the difference in spectra of the products of ozonization and of thermal oxidation shows that the reaction of ozone with natural rubber differs in principle from the thermal oxidative reaction. We suggest that an oxidative chain reaction may occur in both cases, perhaps to widely different extents, and as may be expected yielding quite different end products, since reaction conditions are not similar.

Further evidence for a chain reaction occurring as a component of the ozonization reaction is provided by Zuev²⁷, who found that phenyl-2-naphthylamine was effective in preventing the changes in mechanical properties when ozone reacts with sodium-butadiene rubber.

Measurements of gas uptake during the reaction of ozone with solid natural rubber have been made in an attempt to detect an oxidative chain reaction involving molecular oxygen. Unfortunately the results of measurements by volume change and weight increase methods did not agree. The precise nature of the chain reaction is therefore still unknown.

In addition to the reactions already discussed there is the reaction of further ozone with initial products. The oxozonides of Harries⁸, in which there are more than three oxygen atoms for each original double bond, are formed in this way. The infrared results on the 1170 cm^{-1} band show that such reactions do occur in solid Hevea and Hycar rubbers.

The results obtained in the present work do not provide a ready explanation of why stretched vulcanizates are cracked by ozone. However, the failure of antioxidants to prevent cracking suggests that the reaction which is inhibited by phenyl-2-naphthylamine does not play an important part in the process which leads to cracking. The splitting of the chain at the double bond which has been discussed seems to provide a mechanism for the chain scission which presumably occurs when vulcanizates crack. However, it is possible that the mechanical properties of the film formed at the surface are of more importance in relation to cracking than is any particular reaction. Undoubtedly the fact that the reaction takes place in a very thin layer at the surface is very important in causing cracking. In this connection it is worth noting that the similar cracking caused by free radicals² involves highly reactive chemical species, which probably react at the surface and not in the bulk of the rubber.

The observations on the reaction of air ozonized by an electric discharge with vulcanizates are of interest in relation to accelerated tests of the resistance of vulcanizates to ozone. Since it has been shown that oxides of nitrogen participate in the reaction between air ozonized by an electric discharge and vulcanizates, it seems undesirable to use such a supply of ozone unless the oxides

of nitrogen are removed with caustic soda or are shown to have no influence on crack formation.

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The authors would like to thank D. J. Crisp, Director of the Marine Biological Station, University College of North Wales, for helpful discussion, particularly on the continuous spreading of Hycar monolayers. The authors would also like to thank the Council of The Research Association of British Rubber Manufacturers for permission to publish this work, a report on which was circulated confidentially to members of the Research Association in October, 1953.

SYNOPSIS

The physical changes that occur when ozone reacts with unvulcanized rubber or unstretched vulcanizates have been studied. The speed of reaction is controlled by diffusion of gas into the rubber; as a consequence, initial products formed near the surface are subjected to further action by ozone. To minimize this possibility, experiments have been carried out with thin films of Hevea rubber and monolayers of Hycar OR-15, and the products have been characterized by infrared spectroscopy. The results are considered in relation to observations on the ozonization of simpler compounds recorded in the literature. It is concluded that during ozonization there is a spontaneous scission at the carbon-carbon double bond with the production of aldehyde and (or) ketone and a peroxy biradical. The measurements show the presence of a reaction which is inhibited by 1 per cent phenyl-2-naphthylamine and which is presumably a chain reaction. The nature of this chain reaction is discussed, and it is shown that suppression of this reaction does not prevent the cracking of stretched vulcanizates. The suggestion is made that the characteristic feature of cracking is a reaction which takes place in a thin layer at the surface of the rubber.

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DILAMINAR ELASTOMERIC FILMS *

MYRON G. DEFRIES, LOUIS SCHNEIDER, PAUL FRAM,
AND FRED LEONARD

ARMY PROSTHETICS RESEARCH LABORATORY WALTER REED ARMY MEDICAL
CENTER, WASHINGTON 12, D. C.

INTRODUCTION

While rapid strides have been made in the synthetic organic chemistry of rubberlike materials and in the elucidation of relationships between structure and mechanical properties of elastomers, it is generally not feasible by synthesis alone to construct a rubbery type of polymeric structure which is likely to fulfill all requirements for a given specific application. The tolerances imposed by synthetic methods are very close, and experience indicates that comparatively slight changes in reaction conditions, or monomer, soap, and catalyst concentrations, all may have a profound effect on the balance of properties desired. To aid in the achievement of desired properties, recourse is generally had to compounding. Thus, elastomers are compounded for a variety of reasons. For example, plasticizers are added for improved low-temperature properties, reinforcing agents for improved tensile, tear, and abrasion properties, vulcanizing ingredients for reduced plastic flow and improved elastic recovery, and antioxidants for providing resistance to aging. Furthermore, while optimum combination of synthesis and compounding efforts may achieve adequate bulk properties, the stock may still fail because of surface difficulties, e.g., permanent discoloration on contact with stains, and surface tack development. To overcome these difficulties, in some instances successful use has been made of surface coatings such as talc, waxes, or thin, adherent polymeric films.

In the course of an investigation of latex-dispersed acrylate elastomers intended for casting cosmetic gloves in porous gypsum molds it was found that compounded materials which attained optimum bulk properties developed surface tack when the material, in rubbing against itself under conditions of use, was exposed to cyclic shear and compressive forces. Use of sprayable plastic coatings to overcome this problem was not satisfactory because of adhesion difficulty, loss of mold detail, and development of surface gloss. A technique, termed *dilaminar film casting*, was conceived as a means available to the technologist for imparting specific properties into a rubber compound. An *in situ* method, it comprises the successive deposition of two (or conceivably more) materials on a porous plaster mold surface. The first material is slush-cast in the usual manner and its parent latex removed after sufficient deposition is achieved. A second latex is then substituted before the interface dries, and build-up is continued to the final, desired thickness. Relative thickness of the two layers may be controlled accurately by variation of dwell times. Both male and female molds may be employed for producing dilaminar films.

After drying, curing, and removal from the mold, a laminated structure is obtained in which the outer resistant film is tightly adhered to the soft elastomeric substrate. The surface resistance to staining and to shear and compress-

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sive forces is greatly improved, and gloss-free surface detail of the mold is faithfully duplicated. The purpose of this paper is to describe the preparation of composite elastomeric films, and their physical properties and to indicate the role the technique may play in devising compositions for specific applications.

EXPERIMENTAL

PREPARATION OF SPECIMENS

Synthesis of polymers.—Elastomeric copolymers of butyl acrylate and acrylonitrile (BA/AN) were prepared as previously described¹ by batch emulsion polymerization. A typical charge formula calculated to yield a polymer solids content of 55 per cent is shown below:

Ingredient	Parts by weight
Butyl acrylate and acrylonitrile	100
Santomerse-D	1.23
Potassium persulfate	0.01
Sodium thiosulfate	0.01
Potassium chloride	0.25
Water	82
Sulfuric acid, 10%	0.44

The monomer mixture, emulsifying agent, and water were charged into a 5-liter, 3-necked flask fitted with a stirrer, reflux condenser, and thermocouples. The reactor was flushed with oxygen-free nitrogen, and then the potassium persulfate and sodium thiosulfate were added as separate aqueous solutions. The polymerizations were allowed to proceed at 20–30° C for approximately 24 hours, at which time conversion was over 90 per cent. The latex was vacuum stripped for 1 hour at room temperature.

The purified polymers were analyzed for nitrogen content by the Kjeldahl method.

Latex compounding.—The polyethyl methacrylate (PEMA) reinforcing latex was prepared with the same technique and polymerization system as were the elastomers. Compounding was accomplished by adding the required volume of reinforcing latex to the elastomer latex slowly and with mild agitation, and a pH 8 was obtained by the addition of dilute ammonia.

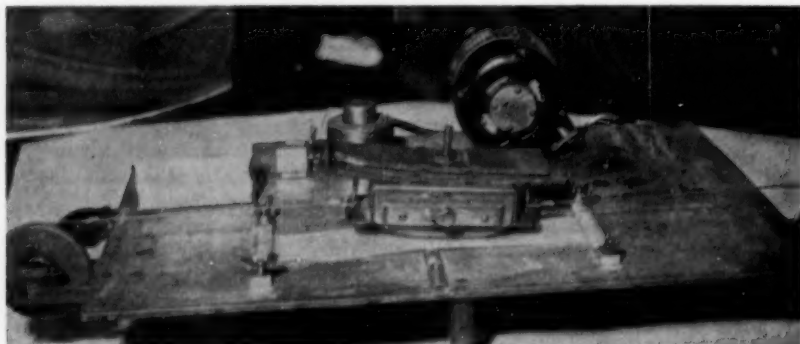


FIG. 1.—Abrasion tester for determining the resistance to surface tack development on repeated rubbing. Note: Trolley is turned sideways in photograph to show mounting of test films. During test, trolley is upright so that the two film surfaces are in flat contact.

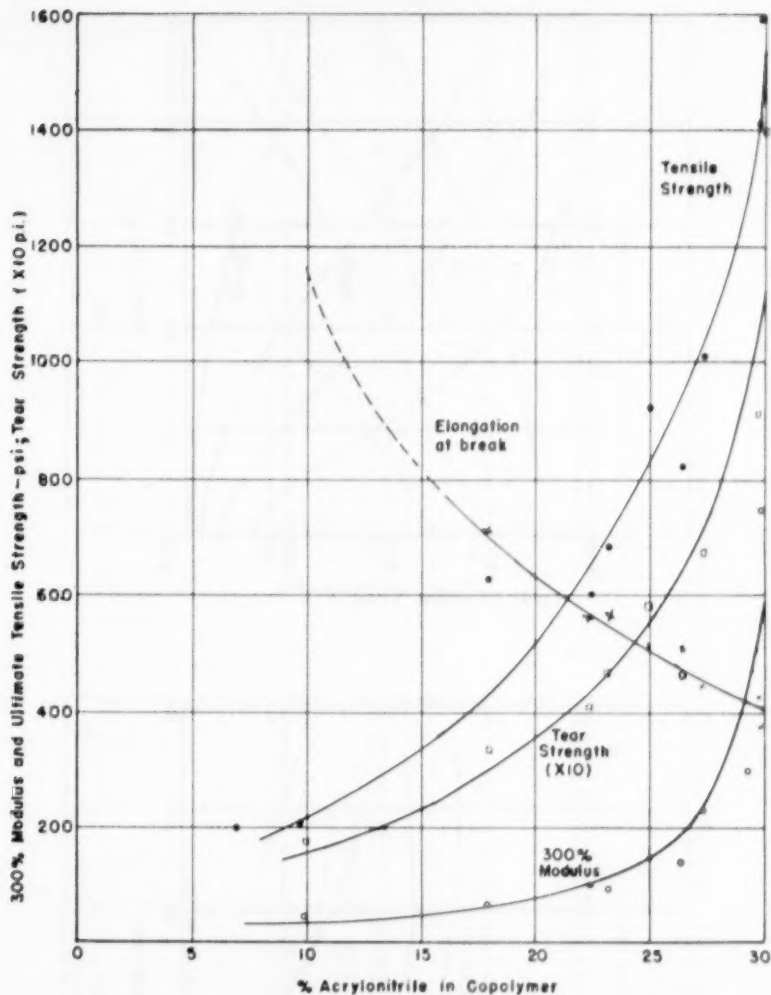
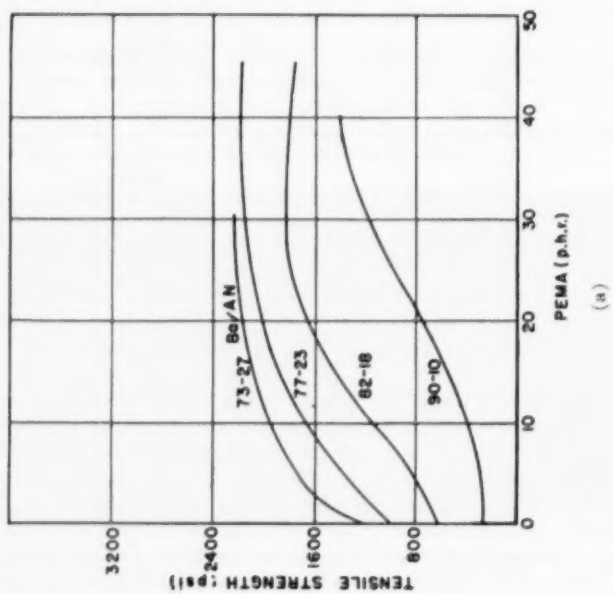
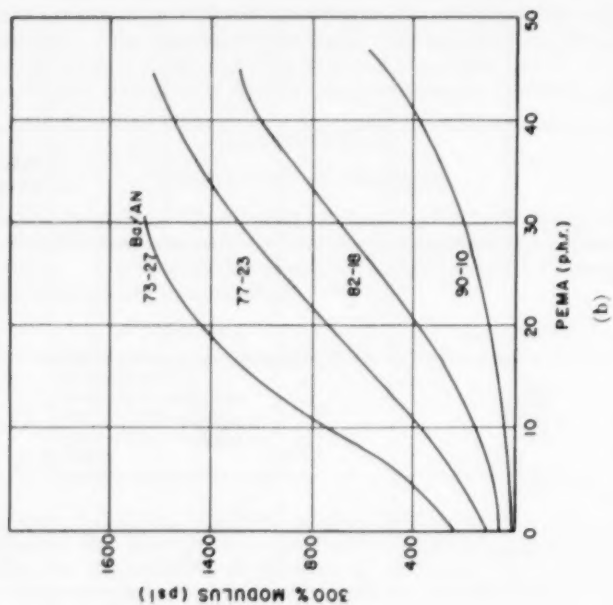
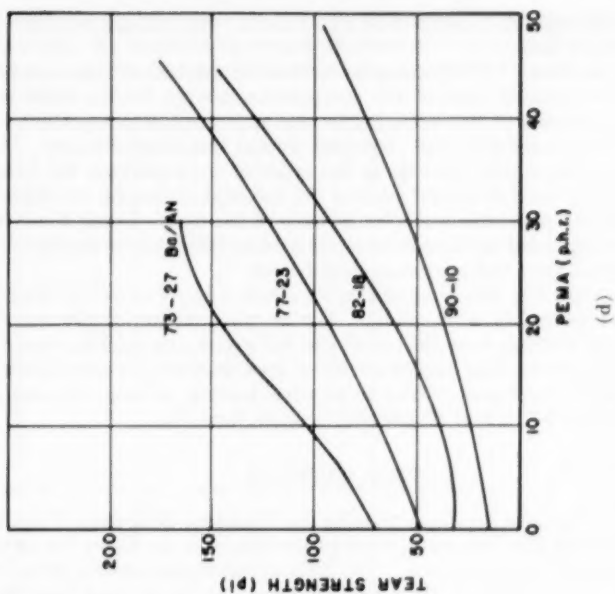


FIG. 2.—Properties of cast films of copolymers of butyl acrylate and acrylonitrile as a function of weight per cent of acrylonitrile in the polymer.

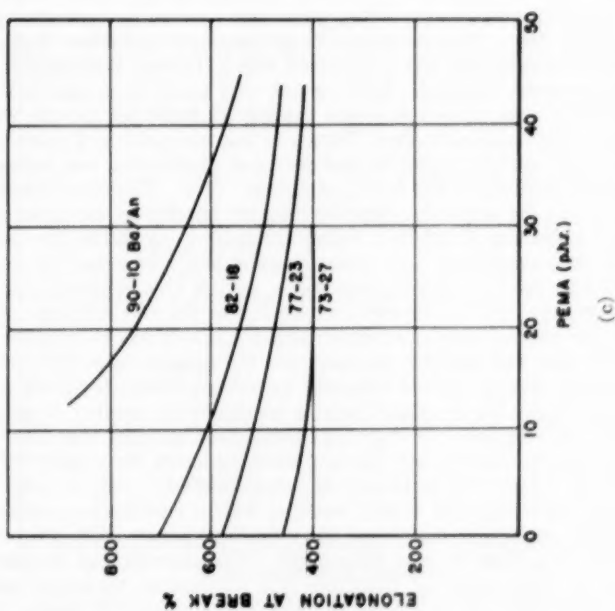
After addition of PEMA, the latexes of BA/AN elastomers containing 10 per cent or less acrylonitrile were further compounded with 6.5 parts of Syton C silica (Monsanto Chemical Co.) and 1.27 parts of benzoyl peroxide in toluene solution per 100 parts of copolymer. No reinforcement other than PEMA was added to the copolymer latexes having more than 10 per cent acrylonitrile.

Description of molds.—Test sheets, 3.75 inches internal diameter and 12 inches long, were cast inside cylindrical stone molds² made from Hydrocal A-11 (U. S. Gypsum Co.). Specimen gloves were cast in female stone molds dupli-





(d)



(c)

FIGS. 3a-3d.—Tensile properties of BA/AN copolymers reinforced with polyethyl methacrylate.

cated from alginate impressions of human hands. Wall thickness of the molds was about 0.375 inch.

Casting procedure.—The procedure for casting dilaminar films consisted of pouring gauze-strained latex of the composition desired for the outer surface slowly down the side of the mold. The rate of pouring was regulated so that no portion of the mold that had once been wetted was allowed to dry. After a predetermined dwell time, usually in the order of 1–10 minutes, the latex was poured from the mold; a second latex of the material chosen for the inner layer was immediately poured in a similar manner to the first. Dwell times for the second layer depended on the rate of build-up and thickness of the film desired. The usual dwell time was approximately 1 hour.

The deposited film was dried *in situ* for about 4 hours at 50° C, after which time it was removed from the mold. For the preparation of flat test sheets, the cylindrical castings were slit parallel to the major axis, and the bottom cut out. The films were then heated at 100° C for 1 hour in a circulating-air oven.

Conditioning of samples.—Prior to physical testing, all samples were conditioned 1 week at 77° F and 50 per cent relative humidity.

TEST METHODS

The tests employed for characterizing the dilaminar films were of two types: one for obtaining the bulk or volume properties, and the other for obtaining properties unique to the surface. The bulk properties measured were 300 per cent tensile stress, ultimate strength, elongation at break, and tear strength using a Scott tester, and low-temperature flexibility using a Tinius-Olsen Stiffness-in-Flexure tester. Test methods were in accord with ASTM procedures D412-49T and D1004-49T, and D747-48T, modified as previously described¹.

For the study of surface properties, tests were devised apropos the specific usage of the end item. The resistance to development of surface tack under shear and compression forces was determined with a Gardner Washability tester (Gardner Laboratory, Bethesda, Md.), which was modified so that mold surfaces of test films were rubbed over one another 32 times per minute with an 8-inch stroke. The moving trolley (Figure 1) was weighted to 2 pounds. In the center of, and at right angles to, the stroke an obstruction was fastened to the instrument table under the lower, stationary film. The obstruction consisted of a 0.5 inch diameter aluminum tubing, cut parallel to the major axis so that the high point was 0.188 inch above the table. As the trolley came in contact with the obstruction, both a compression and a shearing deformation were imparted to the film directly above it. At the area of maximum stress some materials developed tackiness to a degree that the two surfaces could no longer slide over one another, or, in some instances, a hole was worn in the lower film, at which time the test was stopped and the number of cycles recorded. This test correlated with results obtained by cycling cosmetic gloves on mechanical hands under the simulated service condition of grasping objects.

The ability of a material to withstand permanent staining was determined by allowing contact between the film and staining agent for a specified time, and successively attempting to remove the discoloration by wiping with a dry rag, scrubbing with soap and water, washing with a methanol-moistened rag and, finally with an acetone-moistened rag. Staining agents used in these tests were ball-point ink, lipstick, and shoe polish. Discoloration by contact with the products of combustion of cigarettes was determined by laying samples horizontally on a wire grid in a glass chimney and allowing the smoke from a

lighted cigarette tip held 4 inches away to curl over it. A timed air blast was blown through the cigarette to control the rate of burning. Test results were recorded on a comparative basis between the extremes of severe discoloration and none at all.

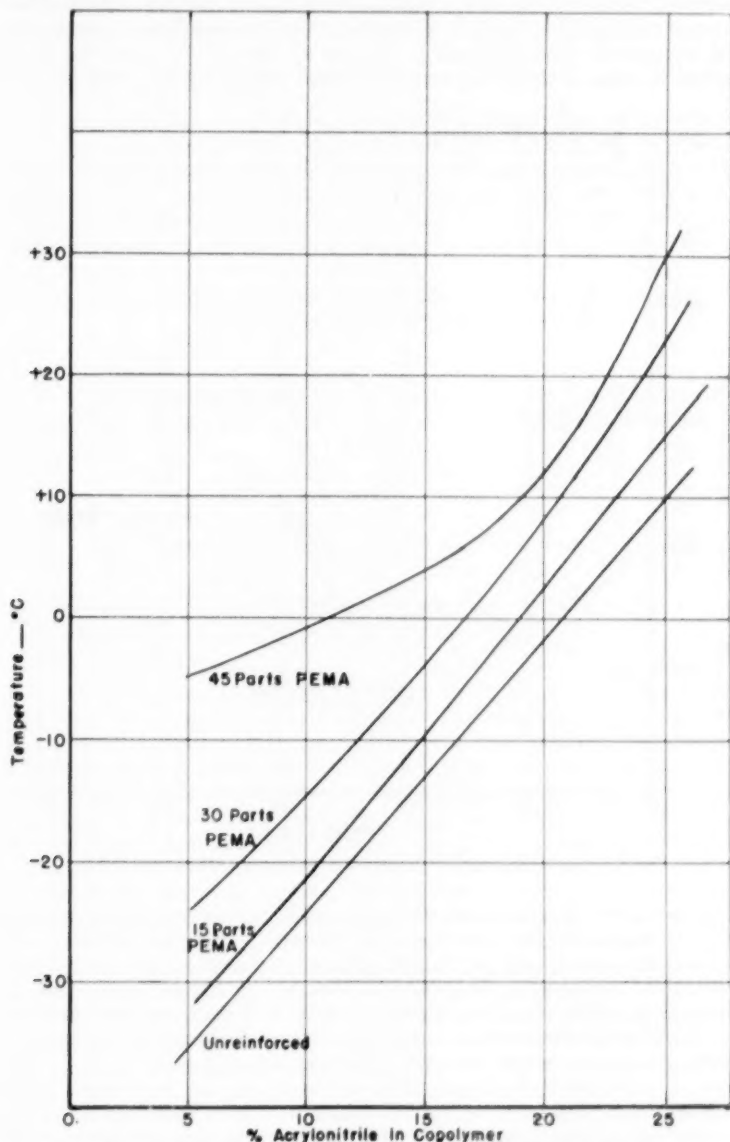


FIG. 4.—Temperature at which the modulus in flexure is 1000 p.s.i. as a function of acrylonitrile content.

RESULTS AND DISCUSSION

HOMOGENEOUS FILMS

Figure 2 shows the properties of cast films of copolymers of butyl acrylate and acrylonitrile as a function of weight per cent of acrylonitrile in the polymer. (The report acrylonitrile contents are calculated values based on the determination of nitrogen in the copolymer.) Figures 3a through 3d show the tensile properties of some of these polymers reinforced with polyethyl methacrylate.

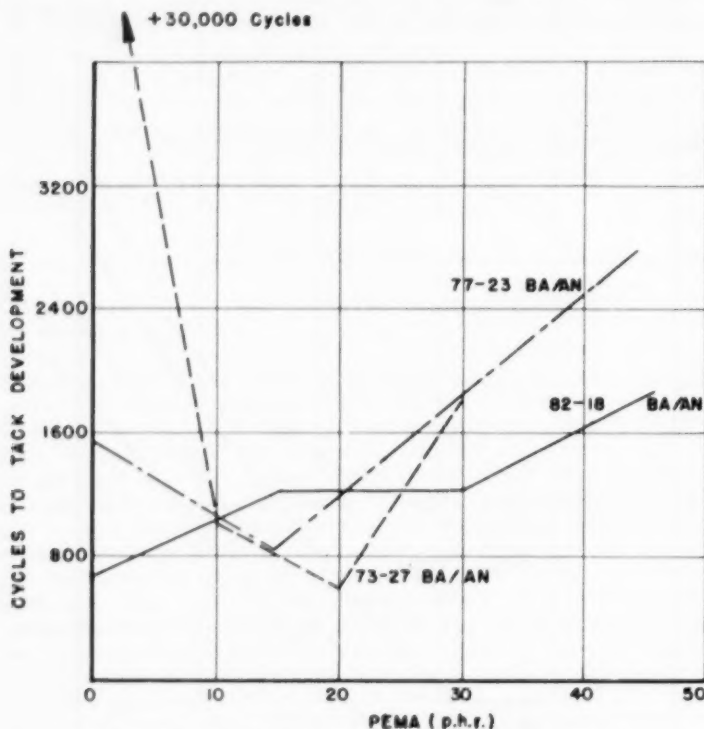


Fig. 5.—Cycles to develop tack vs. polyethyl methacrylate (PEMA) loading.

The enhancement of mechanical properties with increasing acrylonitrile content and increasing reinforcement may be observed. However, as the amount of acrylonitrile content and/or reinforcing agents is increased, the low-temperature flexibility decreases¹. This may be observed in Figure 4 in which the temperature at which modulus in flexure becomes 1000 p.s.i. is plotted as a function of acrylonitrile content and various polyethyl methacrylate loadings.

While room-temperature strength properties are enhanced as the concentrations of acrylonitrile and polyethyl methacrylate are increased, surface properties such as resistance to the development of tack under repeated shear and compression, and resistance to staining and solvents are almost solely responsive to increasing concentration of acrylonitrile. Thus, in Figure 5, at

zero concentration of polyethyl methacrylate, films containing 18 per cent acrylonitrile developed tack after approximately 700 rubs on the Gardner reciprocating machine, compared to 1600 and more than 30,000 rubs for films containing 23 and 27 per cent acrylonitrile, respectively. Furthermore, resistance to irreversible staining by a variety of staining agents was greatly enhanced in the copolymers containing the higher amounts of acrylonitrile.

DILAMINAR FILMS

A series of dilaminar films were cast with a 27 per cent acrylonitrile copolymer composing the surface layer and a 9.5 per cent acrylonitrile copolymer reinforced with 30 parts of polyethyl methacrylate and 6.5 parts of silica as the substrate layer. The properties of these dilaminar films are given in Table I. The rapid thickness build-up during casting of the surface layer of high acrylonitrile material can be seen. In general, it has been observed that a latex disper-

TABLE I
TENSILE PROPERTIES OF DILAMINAR FILMS*

Film	Casting time, min.		Thickness, mils			R^c	300% modulus, psi ^b	Ultimate strength, psi ^b	Elongation, %	Tear strength, psi ^b
	Surface layer	Substrate	Surface	Substrate	Total					
A	0	60	—	38	38	0.00	264	1240	940	82
B	1	59	7.3	49.6	56.9	0.13	236	570	457	59
C	2	58	10.2	48.2	58.4	0.18	220	630	416	58
D	5	55	21.2	33.8	55.0	0.39	277	676	417	55
E	10	50	28.8	28.9	57.7	0.50	264	753	426	50
F	15	45	34.2	24.6	58.8	0.58	240	875	440	45
G	60	0	62	—	62	1.00	236	1040	447	68

* Surface layer: 73:27 butyl acrylate-acrylonitrile copolymer. Substrate: 90.5:9.5 butyl acrylate-acrylonitrile reinforced with 30 parts PEMA and 6.5 parts silica.

^b Calculations of tensile properties based on total thickness of composite film.

^c $R = t_1 / (t_1 + t_2)$.

sion of a hard polymer deposits against a porous gypsum surface faster than a soft one. The relatively slow build-up of soft materials may be attributed to fusion or distortion of individual particles as they deposit against the mold, blocking mass transfer between the latex and the mold wall, preventing deposition via capillary or coagulative means. It is interesting that in the case of the dilaminar films cast during these experiments the actual rate of build-up of the 90:10 BA/AN latex is faster when cast over a layer of harder and fast-depositing material than when cast directly against the mold wall itself.

In the cast dilaminar film the outer surface layer was tightly adhered to the substrate, and the layers appeared to be completely fused. Whether greater adhesion is attainable by this technique because of intermingling of latex particles and mechanical locking during film formation, as compared to solvent deposition or other means, is not known at the present time.

The mechanical properties of the dilaminar films were examined. These, and the properties of the pure components, are compared in Table I. It may be noted that the tensile strength is lower for the dilaminar films than for either pure component, whereas the ultimate elongations of the dilaminar films are about the same as those of the less extensible, homogeneous material. It is believed that the reason for such behavior is the following: At the ultimate elongation of the less extensible material the stress developed in the layer of

greater extensibility is lower than its ultimate. At this elongation the less extensible material snaps, producing a notch and high local stresses, thereby causing the more extensible layer to undergo a tearing failure. According to this mechanism the ultimate elongation of dilaminal films should remain essentially constant at a value equal to that of the less extensible material, independent of laminate thickness, and the ultimate tensile stress of the composite should be lower than that of the stronger component.

Assuming that the over-all tensile resistance of the dilaminal films is due to summation of stresses in each layer at any extension, it is possible to derive a simple formula which may be used to predict the tensile properties of the laminate from the properties of its components:

$$SA = S_1A_1 + S_2A_2 \quad (1)$$

where S is the tensile stress in the dilaminal film and A is the cross-sectional area of the test specimen, and subscripts refer to the individual layers of the dilaminal film. Then, by substituting in Equation (1):

$$A_1 = t_1w, \quad A_2 = t_2w, \quad \text{and} \quad A = (t_1 + t_2)w$$

where t_1 and t_2 are thickness of each lamina, and w is the width of the test specimen:

$$S = (S_1t_1 + S_2t_2)/(t_1 + t_2) \quad (2)$$

Defining the ratio R as: $R = t_1/(t_1 + t_2)$, the following equation relates average stress to stress in each layer:

$$S = R(S_1 - S_2) + S_2 \quad (3)$$

Stresses S_1 and S_2 are the stresses built up in each individual layer at a given elongation.

Figure 6 is a plot of the tensile properties of dilaminal films as a function of the ratio of thickness of outer layer to total thickness. (See Table I for description of the samples.) As predicted by Equation (3), tensile strength of the dilaminal material gives a straight line whose intercept at $R = 1$ is the ultimate strength of the less extensible material, and at $R = 0$ is the stress developed in the more extensible material at the breaking extension. Stresses predicted from the graph are 1080 p.s.i. ultimate for 73:27 material, and 480 p.s.i. for the reinforced 90:10 BA/AN at the breaking elongation of the dilaminal film. This compares to the measured values (Table I) of 1040 and 450 p.s.i., respectively. The 300 per cent modulus of the dilaminal film as a function of R is also a straight line, but of low slope, since the 300 per cent modulus value was approximately the same for the two components of the films used in these experiments.

The flexural moduli as a function of temperature are reported in Table II for the pure components and for the dilaminal films. Initially, two flexural tests were performed on each dilaminal beam, so that each layer was subjected to tension during one test. No significant differences were found. Results reported are for tests in which bending was convex from the surface of stiffer material.

As with the tensile properties, the resistance to flexural deformation of a dilaminal beam under load may be calculated, assuming that it may be treated as an equivalent "T" beam of homogeneous material⁴. The general formula for the ratio of the flexural moduli of a composite beam to that of a beam of the

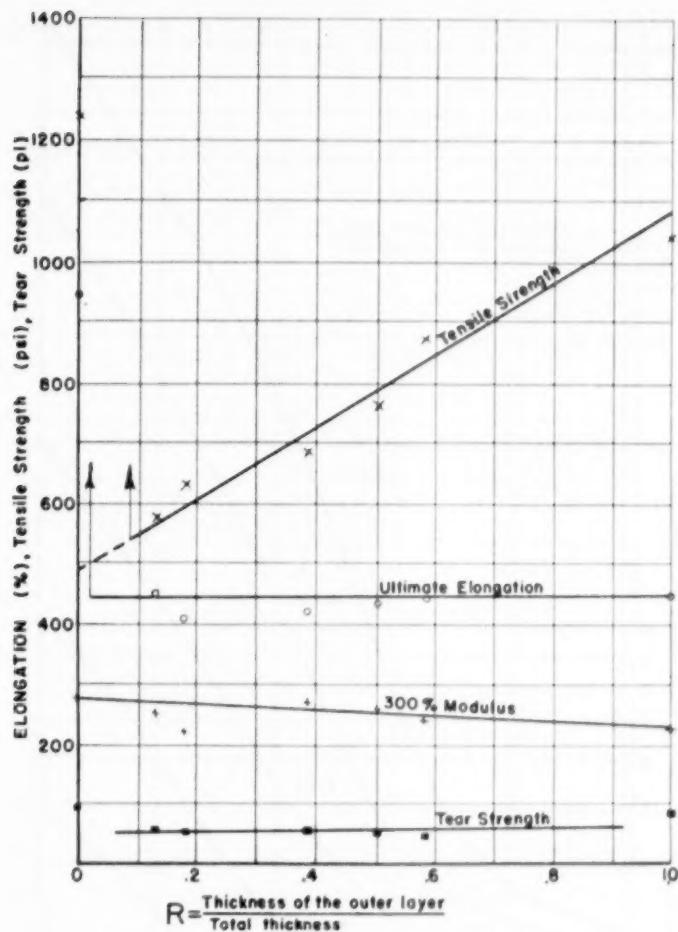


Fig. 6.—Tensile properties of dilaminar films as a function of the ratio of thickness of outer layer to total thickness.

TABLE II
FLEXURAL PROPERTIES OF DILAMINAR FILMS

Film	R^a	Stiffness in flexure modulus (psi) at (° C)					
		+25°	+10°	0°	-10°	-20°	-30°
A	0.00	615	830	980	1,670	4,900	27,500
B	0.13	340	1,550	3,300	5,600	9,600	39,000
D	0.39	330	2,300	5,700	8,400	14,100	51,000
E	0.50	270	2,700	9,000	11,000	17,500	52,000
F	0.58	270	3,300	15,000	21,000	24,000	56,000
G	1.00	190	10,000	57,000	66,000	80,000	84,000

^a $R = t_1 / (t_1 + t_2)$.

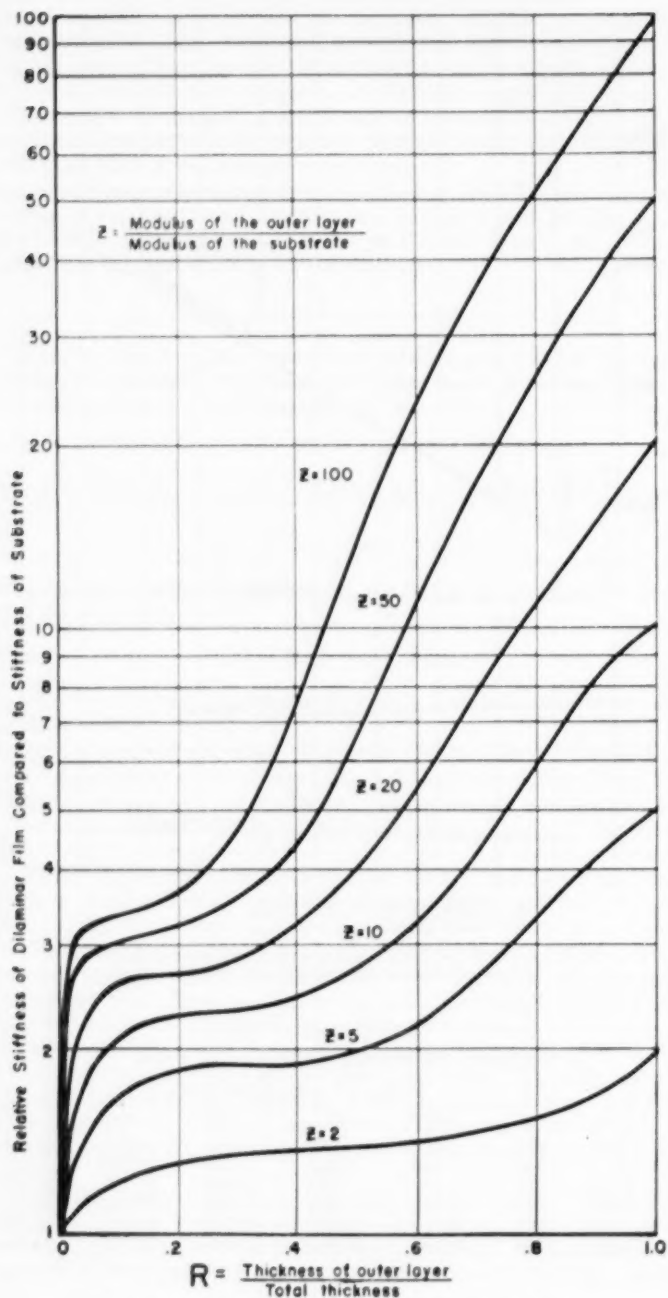


Fig. 7.—Numerical solutions of equations for lamination of materials with stiffness ratios up to 100:1.

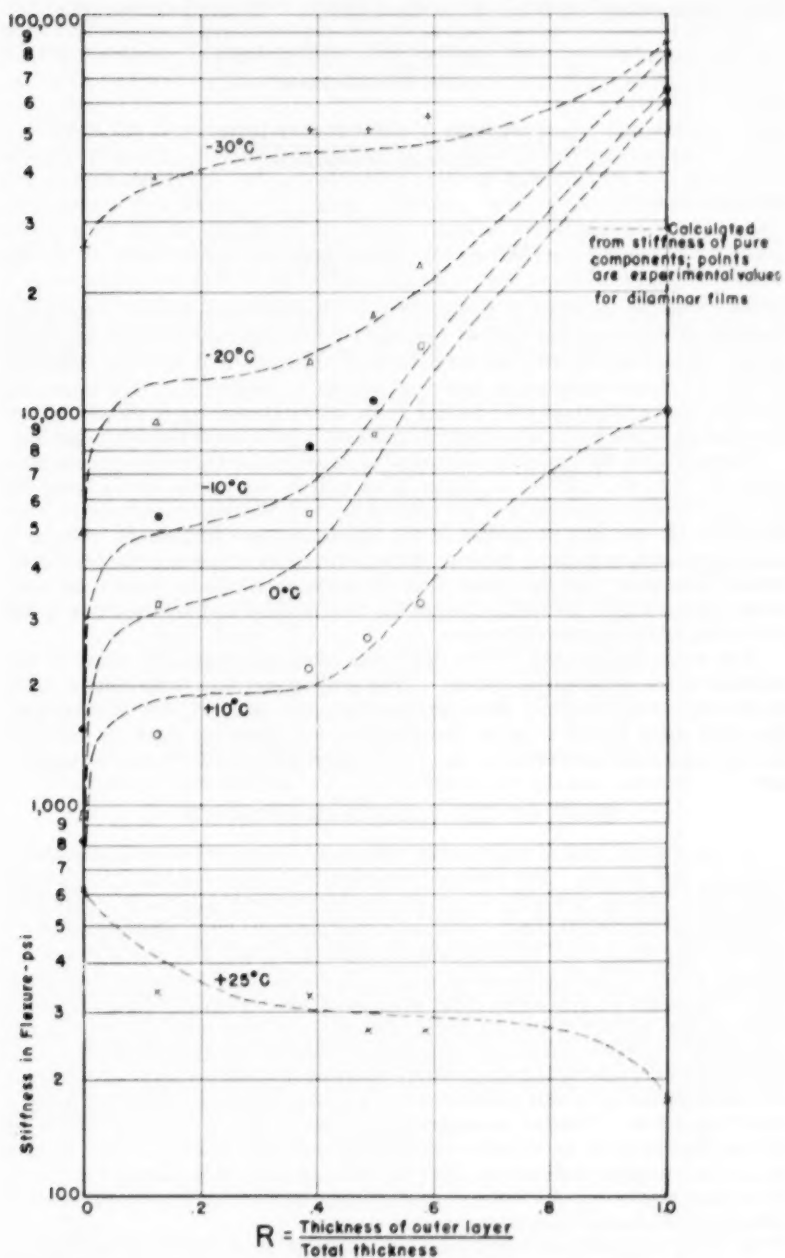


FIG. 8.—Moduli in flexure of the dilaminar films.

lower modulus material is derived in the appendix. In terms of the ratios:

$$R = \frac{\text{thickness of stiffer surface layer}}{\text{total film thickness}}$$

and:

$$Z = \frac{\text{modulus of stiffer surface layer}}{\text{modulus of substrate}}$$

this formula is:

$$\frac{E_D}{E_f} = ZR^3 + (1 - R)^3 + \frac{3(1 - R)ZR}{R(Z - 1) + 1} \quad (4)$$

where E_D is the modulus in flexure of the dilamimar structure and E_f is the modulus of the substrate (softer) material. Numerical solutions of Equation (4) are plotted in Figure 7 for lamination of materials with stiffness ratios up to 100:1. It is of interest to note that an outer material with 100 times the modulus of the substrate may be laid down in thicknesses up to 25 per cent of the total thickness with only a fourfold increase in stiffness of the dilamimar film.

The moduli in flexure of the dilamimar films are plotted over the temperature range of +25 to -30° C in Figure 8, as well as the curves (solid lines) for dilamimar films as a function of the ratio of layer thicknesses as calculated from Equation (4) and the properties of the homogeneous components. There is good agreement, in general, between the experimental values and the calculated values, indicating that dilamimar films of elastomers may be treated as composite beams within the limitations of the test method and assumptions in the derivation of the flexure formula.

The surface properties of the dilamimar films are essentially those of the material of the outer surface layer. Thus a dilamimar film containing a 73:27 butyl acrylate-acrylonitrile copolymer as the outer layer did not develop surface tack after 30,000 rubs on the Gardner reciprocating machine and had solvent resistance ascribable to the 73:27 butyl acrylate-acrylonitrile copolymer.

SCOPE OF THE DILAMIMAR APPROACH

In the general field of engineering materials, dilamimar or composite structures are well known. For example: wooden beams are reinforced with steel strips for enhanced strength; bimetallic temperature regulators are composites of metals of different thermal coefficients of expansion; vinyl plastic-steel composites comprise a material retaining the rigidity of steel and the chemical resistance of the exposed vinyl surface. In the plastics and elastomer materials, the advantages of dilamimar structures have also been exploited. Surface resistant and surface hardened vinyl plastics have been made by solvent extraction of a plasticizer from the surface of a plasticized polyvinyl chloride film, thereby forming a composite structure, consisting of a surface layer of polyvinyl chloride containing smaller quantities and a substrate containing larger quantities of plasticizer. Further examples are composite automobile tires consisting of a surface layer of an abrasion resistant polyurethan elastomer and natural or synthetic rubber substrates. Several patents have been issued describing the surface treatment of a rubber article with chlorine to produce a chlorinated rubber-unchlorinated rubber composite.

In many applications for elastomeric material, it is not at all uncommon to require in a material a set of properties which in theory indicate diametri-

cally opposed synthetic and compounding procedures. For example, if an elastomer is to have good low-temperature properties and at the same time good solvent resistance, increasing the amount of that component which would impart added solvent resistance, results in a loss in low temperature flexibility and vice versa.

Within the copolymer series studied, at one extreme of composition (high acrylonitrile ratio) the elastomer possessed required properties of good abrasion and solvent resistance, but lacked others, such as extensibility, and good low-temperature flexibility. The latter, however, were well achieved at lower acrylonitrile ratios; yet within the entire range of copolymer compositions no entirely satisfactory material was found. Because of such inherent limitations compromises have to be made, and even when one property is partially sacrificed at the expense of another fruition may not be achieved. In this instance, the dilaminal approach has been shown to be of assistance. The properties of two different materials were considered, and the two materials physically com-

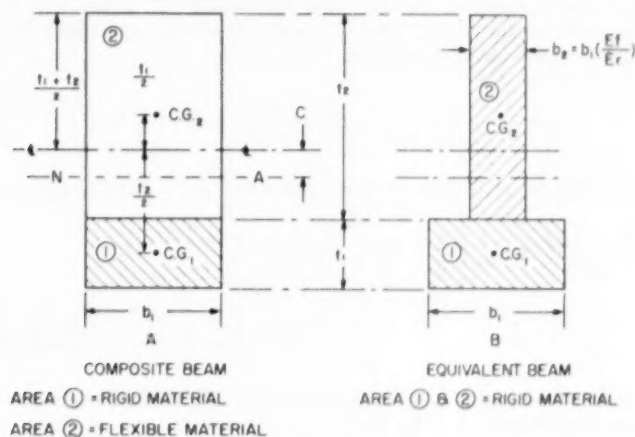


FIG. 9.

bined in juxtaposition to display their individual properties were most effective. By this method, surface properties were realized in an elastomeric composite which were unattainable through the use of a compounded single elastomeric copolymer. It has been shown, however, that even the composite will not completely retain all the optimum properties of its components, and that here, too, as with monolithic structures, some compromise must be accepted. The dilaminal approach then represents one further avenue of compromise, one which may be used with great flexibility, and one which may be used most effectively if the consequences of the physical combination of the elastomers are appreciated.

APPENDIX

DERIVATION OF EQUATION FOR STIFFNESS IN FLEXURE OF COMPOSITE BEAMS

It is assumed that the composite beam may be replaced by an equivalent "T" beam of homogeneous material as shown in Figure 9.

A. Determination of the Neutral Axis of Composite Beam

The location of the plane of the neutral axis is such that the first moment of area (1) is equal to that of area (2):

Distance C.G.₂ to N.A. \times area (2) = distance C.G.₁ to N.A. \times area (1)

$$\left[\frac{t_1}{2} + c \right] b_2 t_2 = \left[\frac{t_2}{2} - C \right] b_1 t_1 \quad \therefore C = \frac{t_1 t_2}{2} \left[\frac{b_1 - b_2}{b_1 t_1 + b_2 t_2} \right] \quad (1)$$

B. Determination of the Second Moment of Composite Beams

$$I_E = I_{(1)} + A_{(1)} (\text{distance C.G.}_1 \text{ to N.A.})^2 + I_{(2)} + A_{(2)} (\text{distance C.G.}_2 \text{ to N.A.})^2$$

where I_E is the moment of inertia of the equivalent "T" beam, and I_1 and I_2 are moments of inertia of the areas (1) and (2) of the equivalent "T" beam about their center lines, respectively.

$$I_E = \frac{t_1^3}{12} + b_1 t_1 \left(\frac{t_2}{2} - C \right)^2 + \frac{b_1 t_1^3}{12} + b_2 t_2 \left(\frac{t_1}{2} + C \right)^2$$

Substituting for C as defined in Equation (1) and collecting terms:

$$I_E = \frac{b_1 t_1^3 + b_2 t_2^3}{12} + b_1 t_1 \left[\frac{t_2}{2} - \frac{t_1 t_2}{2} \left(\frac{b_1 - b_2}{b_1 t_1 + b_2 t_2} \right) \right]^2 + b_2 t_2 \left[\frac{t_1}{2} + \frac{t_1 t_2}{2} \left(\frac{b_1 - b_2}{b_1 t_1 + b_2 t_2} \right) \right]^2 \quad (2)$$

The second moment of a homogeneous beam of rectangular cross section of width b_2 and thickness $(t_1 + t_2)$ is:

$$I_r = \frac{1}{12} b_2 (t_1 + t_2)^3$$

$$\frac{I_E}{I_r} = \frac{b_1 t_1^3 + b_2 t_2^3}{b_2 (t_1 + t_2)^3} + \frac{1/4 b_1 t_1 t_2^2}{\frac{1}{12} b_2 (t_1 + t_2)^3} \left[1 - \frac{t_1 (b_1 + b_2)}{b_1 t_1 + b_2 t_2} \right]^2 + \frac{1/4 b_2 t_2 t_1^2}{\frac{1}{12} b_2 (t_1 + t_2)^3} \left[1 + t_2 \left(\frac{b_1 - b_2}{b_1 t_1 + b_2 t_2} \right) \right]^2 \quad (3)$$

Defining:

$$Z = b_1/b_2 = E_r/E_f$$

where E_r is the modulus of elasticity of the rigid material and E_f is the modulus of elasticity of the flexible material.

$$R = \frac{t_1}{t_1 + t_2} \left(\text{and } \frac{t_2}{t_1 + t_2} = 1 - R \right)$$

then:

$$\begin{aligned}
 1 - t_1 \left(\frac{b_1 - b_2}{b_1 t_1 + b_2 t_2} \right) &= 1 - R(t_1 + t_2) \left[\frac{b_1 - b_2}{b_1 R(t_1 + t_2) + b_2(1 - R)(t_1 + t_2)} \right] \\
 &= 1 - R \left[\frac{b_1 - b_2}{b_1 R + b_2(1 - R)} \right] \\
 &= 1 - R \left[\frac{Z - 1}{ZR + (1 - R)} \right] \\
 &= \frac{ZR + 1 - R - RZ + R}{ZR + (1 - R)} \\
 &= \frac{1}{R(Z - 1) + 1} \quad (3a)
 \end{aligned}$$

$$\begin{aligned}
 1 + t_2 \left(\frac{b_1 - b_2}{b_1 t_1 + b_2 t_2} \right) &= 1 + (1 - R) \left(\frac{b_1 - b_2}{b_1 R + b_2(1 - R)} \right) \\
 &= 1 + \frac{(1 - R)(Z - 1)}{ZR + (1 - R)} \\
 &= \frac{R(Z - 1) + 1 + (1 - R)(Z - 1)}{R(Z - 1) + 1} \\
 &= \frac{Z}{R(Z - 1) + 1} \quad (3b)
 \end{aligned}$$

Substituting (3a) and (3b) in (3):

$$\begin{aligned}
 \frac{I_E}{I_r} &= ZR^3 + (1 + R)^3 + 3ZR(1 - R)^2 \left(\frac{1}{R(Z - 1) + 1} \right)^2 \\
 &\quad + 3(1 - R)R^2 \left(\frac{Z}{R(Z - 1) + 1} \right)^2 \\
 \frac{I_E}{I_r} &= ZR^3 + (1 + R)^3 + \frac{3ZR(1 - R)}{R(Z - 1) + 1} \left(\frac{(1 - R) + ZR}{R(Z - 1) + 1} \right) \\
 \frac{I_E}{I_r} &= ZR^3 + (1 - R^3) + \frac{3ZR(1 - R)}{R(Z - 1) + 1} \quad (4)
 \end{aligned}$$

In Equation (4) I_E is the moment of inertia of a "T" beam of equivalent stiffness to the dilaminar beam, when the "T" beam is composed of rigid material, i.e.:

$$(EI)_{\text{"T" beam}} = (EI)_{\text{dilam. beam}}$$

(see ASTM, Standards Part 6, 1952, p. 650). Then:

$$E_r \cdot I_E = E_D \cdot I_f$$

where $I_f = 1/12b_1(t_1 + t_2)^3$, or:

$$\frac{E_D}{E_r} = \frac{I_E}{I_f} = \frac{I_E}{\frac{1}{12} b_1 (t_1 + t_2)^3}$$

since:

$$b_1/b_2 = E_r/E_f$$

$$\frac{E_D}{E_r} = I_E / \frac{1}{12} \frac{E_r b_2 (t_1 + t_2)^3}{E_f}$$

$$E_D/E_f = I_E / 1/12 b_2 (t_1 + t_2)^3 = I_E/I_r$$

$$\frac{E_D}{E_f} = ZR^3 + (1 - R)^3 + \frac{3ZR(1 - R)}{R(Z - 1) + 1} \quad (5)$$

SYNOPSIS

Many applications of rubberlike materials require a combination of bulk and surface properties which may not be attained with a specific elastomeric composition, regardless of vulcanization, reinforcement, or other modification by compounding, but may be achieved by combining two materials in a laminated structure. This paper describes a technique for casting hollow laminated elastomeric structures from aqueous dispersions in molds of plaster of Paris. An elastomeric composition which has the properties required of the surface is deposited first, and a second composition having the properties required of the bulk is then cast against the original film before the latter dries in the mold. This process, termed "dilaminar" film casting, yields laminated films having resistant surface layers of uniform controllable thickness that are inherently bound to the substrate. The properties of a series of butyl acrylate-acrylonitrile copolymers of varying monomer ratios and amounts of organic reinforcing agents were studied. It was found that unreinforced copolymers of approximately 27-30 per cent acrylonitrile had suitable resistance to staining and abrasion, while reinforced compositions of an elastomer copolymer having an acrylonitrile content of about 10 per cent displayed optimum bulk but poor surface properties. Dilaminar films were cast of two compositions having optimum properties for surface and substrate layers. The laminated films retained the surface resistance of the outer laminas and exhibited mechanical properties intermediate between the properties of the two components. Equations relating tensile and flexural properties of laminated elastomeric films to those of the single homogeneous compositions were derived, and calculated tensile and flexural values were found to agree with the experimental data.

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ISOTOPE EXCHANGE BETWEEN SULFUR ATOMS IN VULCANIZATION ACCELERATORS IN THE PRESENCE OF DIPHENYLGUANIDINE AND PHENYL-2-NAPHTHYLAMINE *

G. A. BLOKH, E. A. GOLUBKOVA, AND K. V. KURSKAYA

F. E. DZERZHINSKIĖ CHEMICAL-TECHNOLOGICAL INSTITUTE, DNEPROPETROVSK, U.S.S.R.

In previous work¹ it was shown that in the process of vulcanization a continual series of isotope exchange reactions takes place between the sulfur atoms in the various sulfur-containing ingredients of the vulcanizate. It was established that the sulfur atoms which enter into this isotope exchange include not only those which go into the structure of the molecule of accelerator, e.g., mercaptobenzothiazole, benzothiazolyl disulfide, and tetramethylthiuram disulfide, carbamates, and sulfenamides, but also the sulfur atoms which form the polysulfide bonds, $R-S_m-R$, and, in addition, those present in the form of secondary products formed in the vulcanization process (hydrogen sulfide and zinc sulfide). Evidently the exchange reactions between sulfur atoms in the substances present in an accelerator-type vulcanization, in which sulfur in a reactive form is liberated, and active radicals are formed from the accelerator and take part in structure formation in the rubber, are of prime importance. The formation of a vulcanization network in which the rubber, sulfur, and carbon black are chemically combined, is another result of industrial vulcanization.

It is known that amine products containing no sulfur, e.g., diphenylguanidine and phenyl-2-naphthylamine, as well as zinc oxide and other materials, also enter into the composition of a rubber vulcanizate. Hence it is of practical importance to clarify also the effect of the various nonsulfur-containing ingredients of a rubber stock on the intensity of the isotope exchange between the sulfur atoms in the substances taking part in the accelerated vulcanization of rubber.

It was shown earlier² that the presence of zinc oxide retards the isotope exchange between the sulfur atoms of mercaptobenzothiazole and those of elemental sulfur; this was explained by the formation of a zinc salt of mercaptobenzothiazole, and the inability of this salt to undergo a tautomeric change into mercaptobenzothiazole with a thionic structure. What, then, might be the effect on the intensity of isotope exchange of such important ingredients as the aging inhibitor, phenyl-2-naphthylamine, or the nonsulfur-containing accelerator diphenylguanidine?

The role of diphenylguanidine as an accelerator of moderate strength has been described in the literature³. It is known that a combination of diphenylguanidine and mercaptobenzothiazole forms a stronger accelerator combination than either of them taken separately. The mechanism of the action of this accelerator combination has not been investigated sufficiently. The reaction mechanism is usually ascribed to the formation of an unstable saltlike complex

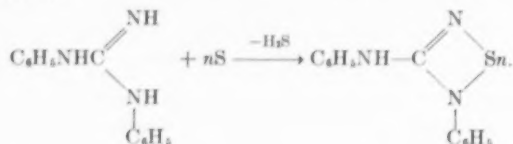
* Translated from RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from the *Doklady Akademii Nauk S.S.S.R.*, Vol. 105, No. 2, pages 275-278 (1955).

which decomposes on further heating. However, no such reaction between diphenylguanidine and sulfur has been observed under these conditions.

Our data⁴ and those of other authors⁵ show that the most effective accelerators are also those that undergo the most intensive sulfur isotope exchange at lower temperatures. Thus, while mercaptobenzothiazole after 3 hours' heating at 100° C shows practically no exchange with elemental sulfur, nevertheless Thiuram at 100° or potassium xanthate at room temperature enters into an intensive isotope exchange reaction with sulfur. Hence the isotope exchange data agree with the industrial characteristics of the accelerators mentioned. It may be assumed at the outset that, if isotope exchange is one of the characteristics of an accelerator's effectiveness, then a more intense sulfur isotope exchange should occur between sulfur and mercaptobenzothiazole when diphenylguanidine is present, since a combination of these accelerators gives stronger acceleration.

We studied the kinetics of this exchange at 100° and 125° C. A mixture of the sulfur radioisotope, mercaptobenzothiazole and diphenylguanidine in the ratio 2:1:1, respectively, was dissolved in xylene and placed in ampoules, which were then sealed and heated at 100° C for periods of 3, 4, 5, 8, 10, and 18 hours and at 125° for 3, 5, 8, and 10 hours. The ampoules were then opened, and the mercaptobenzothiazole was separated with an aqueous sodium hydroxide solution and then reprecipitated with hydrochloric acid. The residue left after the alkali treatment was then treated with cold alcohol, and in this way the radioisotope was separated from the diphenylguanidine. The diphenylguanidine and its reaction products with sulfur went into the alcohol extract; the radio-sulfur was recrystallized from benzene. Finally, each of the above components was tested for radioactivity in an end-window Geiger counter for the detection of soft β -radiation. The results of the isotope exchange between the sulfur atoms of the mercaptobenzothiazole and those of the elemental sulfur in the presence of diphenylguanidine are presented in Table 1.

As is seen from the data presented, the sulfur isotope exchange increases markedly in the presence of diphenylguanidine, both at 100° and at 125° C, during the whole period of time. Of considerable interest is the fact that the diphenylguanidine separated by the alcohol extraction showed radioactivity. This by itself attests to the existence of a reaction between diphenylguanidine and sulfur, with the formation of a polysulfide compound of diphenylguanidine; apparently this compound also enters into a sulfur isotope exchange in the vulcanization process.



A different situation was noted, however, in a study made by us of the kinetics of sulfur isotope exchange between mercaptobenzothiazole and elemental sulfur in the presence of an antioxidant, namely, phenyl-2-naphthylamine. The importance of phenyl-2-naphthylamine as an aging inhibitor and the part that it plays in the oxidation and vulcanization processes has been adequately discussed in the literature⁶. However in none of this work was the question raised as to a possible reaction between phenyl-2-naphthylamine and elemental sulfur, with the formation of a sulfurized phenyl-2-naphthylamine

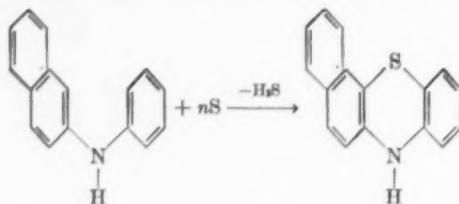
TABLE I
KINETICS OF THE ISOTOPE EXCHANGE BETWEEN THE SULFUR ATOMS OF MERCAPTOBENZOTHAZOLE AND OF
ELEMENTAL SULFUR IN THE PRESENCE OF DIPHENYLGUANIDINE

Weight in milligrams		Temperature (°C)	Duration of exchange (hrs.)	Radioactivity (counts/min./mg.)			Exchange (per cent)	Radioactivity of diphenyl- guanidine (counts/min.)
Mercapto- benzothiazole	Diphenyl- guanidine			Original elemental sulfur	Equilibrium elemental sulfur	Sulfhydryl sulfur in mercapto- benzothiazole		
150.0	—	100	3	1803	1644	15	0.9	—
150.0	153.0	100	3	1803	1644	34	2.1	100
150.2	—	100	4	1328	1211	21	1.7	—
150.4	150.2	100	4	1349	1230	174	14.1	41
150.0	—	100	5	1417	1292	36	2.8	—
150.0	150.0	100	5	1417	1292	123	9.5	121
150.0	—	100	8	1428	1302	41	3.1	—
150.0	151.4	100	8	1349	1230	158	12.8	49
150.0	—	100	10	1803	1644	86	5.2	—
150.0	150.5	100	10	1803	1644	350	21.3	73
150.0	—	100	18	1789	1631	112	6.8	—
150.0	150.3	100	18	1789	1631	480	29.4	114
150.0	—	125	3	1307	1195	91	8.7	—
150.0	150.0	125	3	1143	1042	247	23.7	—
150.0	—	125	5	1246	1139	208	20.0	—
151.3	151.3	125	5	1143	1042	486	46.6	—
150.0	—	125	8	1246	1139	642	62.6	—
150.0	153.3	125	8	1142	1042	800	76.8	—
150.0	—	125	10	1237	1131	647	62.1	—
150.0	100.2	125	10	1142	1042	1026	98.4	—

compound, nor as to the effect of this secondary product on the protection of rubber from oxidation or on the vulcanization process.

We made a study of the kinetics of the exchange of sulfur atoms between mercaptobenzothiazole and elemental sulfur in the presence of the antioxidant, phenyl-2-naphthylamine, these being present in the ratio 1:2:1, respectively. The above combination of active ingredients was dissolved in 20 ml. of xylene and heated in sealed ampoules at 100° and 125° C for periods of 3, 4, 5, 8, 10, and 18 hours. The separation of the free radiosulfur from the other components was carried out by the method described above. The phenyl-2-naphthylamine, which was separated by alcohol extraction, was then heated in alcoholic alkali solution for the purpose of separating from the phenyl-2-naphthylamine any benzothiazolyl disulfide which might possibly be formed under our test conditions, the presence of which might very well distort the true situation regarding the sulfurization of phenyl-2-naphthylamine, if this did occur at all. Finally, each of the components separated was tested for radioactivity. The kinetics of the sulfur isotope exchange in the presence of the antioxidant phenyl-2-naphthylamine is presented in Table 2.

From the data given, one may conclude that phenyl-2-naphthylamine has practically no effect on the intensity of the isotope exchange; in this its behavior markedly differs from that of diphenylguanidine. Another noteworthy fact which we observed was that the phenyl-2-naphthylamine separated by alcoholic extraction after triple recrystallization possessed radioactivity. This unquestionably indicates that there is a reaction between the radiosulfur and the phenyl-2-naphthylamine, i.e., that the phenyl-2-naphthylamine has become sulfurized. We may assume that the observed fact of the formation of a sulfur compound of phenyl-2-naphthylamine (possibly of the benzophenethiazine type) is of prime importance, from the standpoint of either its protective properties or its effect upon the kinetics of vulcanization.



In another set of special experiments we heated sulfur with diphenylguanidine and sulfur with phenyl-2-naphthylamine, both in a 1:1 ratio, in glass ampoules at 141° C for 120 minutes. The hydrogen sulfide liberated was collected in iodine and the solution titrated with thiosulfate. In the experiments with sulfur and diphenylguanidine, 0.074 per cent of the sulfur originally present was liberated as hydrogen sulfide, whereas with sulfur and phenyl-2-naphthylamine, 0.64 per cent was liberated.

Hence, when one considers the oxidative processes in sulfur vulcanizates, it is necessary to bear in mind not only the reaction of sulfur with the oxygen-containing portions of the molecular chains in the rubber, but also its reaction with the antioxidant; i.e., the sulfurizing of the latter. Hence, the consumption of phenyl-2-naphthylamine may result not only from reactions with the peroxide radicals in the rubber, but also from reactions with free sulfur or with sulfur liberated by the decomposition of polysulfide bonds in the vulcanizate.

TABLE 2
KINETICS OF SULFUR ISOTOPE EXCHANGE BETWEEN MERCAPTOBENZOTHAZOLE AND ELEMENTAL SULFUR
IN THE PRESENCE OF PHENYL-2-NAPHTHYLAMINE

Sample weight in milligrams		Radioactivity (counts/min./mg.)					Duration of exchange (hrs.)	Temperature (°C)	Phenyl-2-naphthylamine	Radioactivity (counts/min.)		
Mercapto-benzothiazole	Sulfur	Original elemental sulfur	Equilibrium elemental sulfur	Sulfhydryl sulfur in mercapto-benzothiazole	Exchange (per cent)	of phenyl-2-naphthylamine (counts/min.)						
150.8	300.0	1724	1576	19	1.1	—						
150.2	300.0	1724	1575	19	1.1	—						
150.0	300.0	1328	1214	16	1.3	—						
150.0	300.0	1328	1214	8	0.7	—						
150.0	300.0	1417	1296	26	2.0	—						
150.0	300.0	1540	1408	23	1.6	—						
150.2	300.0	1528	1397	52	3.7	—						
150.2	300.0	1528	1397	55	3.9	—						
150.0	300.0	1710	1564	66	4.2	—						
150.4	300.0	1710	1564	105	6.7	—						
150.6	300.0	1697	1551	73	4.7	—						
150.0	300.0	1697	1551	92	5.9	42						
150.0	300.0	1307	1195	111	9.2	—						
150.0	300.0	1307	1195	95	7.9	22						
150.0	300.0	1246	1139	232	20.3	—						
150.0	300.0	1246	1139	337	29.5	38						
150.0	300.0	1246	1139	721	63.3	—						
150.0	300.0	1246	1139	705	61.8	20						
150.0	300.0	1237	1131	715	63.2	—						
150.0	300.0	1237	1131	710	62.7	50						
—	300.0	1021	—	—	—	27						
—	300.0	1029	—	—	—	25						
—	300.0	1029	—	—	—	78						
—	300.0	1028	—	—	—	209						

It is evident that the phenyl-2-naphthylamine, by attracting part of the sulfur to itself, reduces the concentration of the free sulfur which participates in the creation of vulcanization junctions in the rubber. In the light of this, one may understand why vulcanizates containing phenyl-2-naphthylamine have a lower tensile strength at optimum cure than vulcanizates without an antioxidant.

The products of reactions between sulfur and diphenylguanidine and between sulfur and phenyl-2-naphthylamine undoubtedly exert an influence on the isotope exchange in the process of rubber oxidation.

ACKNOWLEDGMENT

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REACTION OF ELEMENTAL SULFUR AND MERCAPTOBENZOTHAZOLE *

G. A. BLOKH, E. A. GOLUBKOVA, AND G. P. MIKLUKHIN

L. V. PISARENHOVSKIĬ INSTITUTE OF PHYSICAL CHEMISTRY OF THE ACADEMY OF SCIENCES
OF THE U.S.S.R. AND THE KIEV TECHNOLOGICAL INSTITUTE OF LIGHT INDUSTRY,
KIEV, U.S.S.R.

INTRODUCTORY

One of the most important problems in the field of the physics and chemistry of rubber is that of vulcanization. Until now no single theory has been established, which elucidates the complex physico-chemical changes which occur during this process. Still more obscure has been the mechanism of the action of vulcanization accelerators, which, as is well known, not only reduce the time and the temperature of vulcanization, but also influence the physico-mechanical and chemical properties of the rubber¹. Most investigators have assumed that in the acceleration process a reaction with sulfur converts it to an active form which is capable of bringing about vulcanization at a lower temperature and at a greater rate, than with ordinary elemental sulfur in the absence of an accelerator. This point of view is based on the experimental fact that the vulcanization of rubber by sulfur dioxide and hydrogen sulfide, for example, which form sulfur in the nascent condition, proceeds rapidly even at room temperature.

Investigators have also assumed that in the vulcanization process activation of sulfur in the presence of accelerators may occur by different mechanisms. It is possible that the accelerator, reacting with elemental sulfur, forms unstable intermediate compounds, which decompose with liberation of sulfur in an active form. The latter reacts with rubber, and the regenerated accelerator reacts again with elemental sulfur, etc. However, a different process is possible for the activation of elemental sulfur. By this second mechanism the unstable combination of accelerator and sulfur reacts directly with rubber without the formation of active sulfur.

Both these mechanisms necessarily assume the formation of intermediate unstable combinations of the accelerator with sulfur. However, direct, experimentally-based demonstrations of such an interaction are lacking in the literature. There exist only theoretical hypotheses concerning the nature of the possible intermediate combination of the accelerator with sulfur. According to Ostromislensky's concepts², further developed by Bedford³, such an intermediate compound has the character of a polysulfide. According to Bruni and Romani⁴, this intermediate compound is a disulfide. As is well known, the disulfide theory was placed in doubt by Zaide and Petrov⁵ on the basis of data from the vulcanization of rubber in the presence of benzothiazolyl disulfide.

GENERAL

The present work was undertaken with a view to confirming experimentally the formation of intermediate compounds between mercaptobenzothiazole and

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elemental sulfur, in which all the sulfur atoms or a definite portion of them would be *interchanged*, that is, made chemically equivalent. This problem may be investigated with the help of the method of labelled atoms. In order to solve this problem, we studied the exchange reaction of sulfur atoms between mercaptobenzothiazole and elemental sulfur in fusion mixtures solutions, and rubber mixtures under vulcanization temperature conditions.

EXPERIMENTAL

STUDY OF EXCHANGE IN SULFUR-MERCAPTOBENZOTHIAZOLE MIXTURES

Mixtures of powdered radioactive sulfur and chemically pure mercaptobenzothiazole were fused at temperatures of 145°, 150°, and 154° (temperature fluctuations did not exceed $\pm 1^\circ$), and also subjected to heat treatment at a

TABLE I
EXCHANGE REACTION BETWEEN MERCAPTOBENZOTHIAZOLE AND
RADIOACTIVE SULFUR IN THEIR MIXTURES AND FUSION MIXTURES*

No. of experiment	Time (min.)	Temperature (°C)	Exchange (%)
1	30	100°	0
2	60	100°	1
3	180	100°	1
4	5	145°	28
5	10	145°	31
6	15	145°	44
7	30	145°	44
8	60	145°	48
9	240	145°	76
10	3	150°	31
11	10	150°	44
12	30	150°	52
13	60	150°	58
14	3	154°	31
15	5	154°	46
16	67	154°	74
17	180	154°	88

* Similar results were obtained in a study of the counter exchange between ordinary elemental sulfur and mercaptobenzothiazole labelled with radioactive sulfur.

temperature of 100° for different time intervals. After heating, the mixtures were cooled rapidly to room temperature, and from the resulting fusion the mercaptobenzothiazole was separated by treatment in the cold with a 1 per cent aqueous solution of sodium hydroxide, followed by decomposition of the sodium salt of mercaptobenzothiazole with hydrochloric acid. The mercaptobenzothiazole thus separated had a m.p. of 178–179°. The results of measurements of the activity of mercaptobenzothiazole are given in Table I. The sulfur which remained on the filter was found to be somewhat colored, but we did not purify it further; its activity was not measured. Experiments were set up separately for the reverse exchange of inactive elemental sulfur and mercaptobenzothiazole labelled with radioactive sulfur.

STUDY OF THE EXCHANGE OF SULFUR WITH MERCAPTOBENZOTHIAZOLE

Studies were made with natural rubber (light crepe), previously deresinified by prolonged extraction of the resinous compounds with acetone. After the

addition of radioactive sulfur and mercaptobenzothiazole to the purified rubber, the rubber mixtures were vulcanized in an electric press at temperatures of 145° and 150° C, under a hydraulic pressure of 120 atm., for different periods of time from 15 to 180 minutes, i.e., under conditions which assured thorough vulcanization. The resulting vulcanized films, 0.1–0.2 mm. thick, were ground fine and extracted with acetone for a long time in order to separate the free sulfur and mercaptobenzothiazole from the vulcanizate. The subsequent separation of mercaptobenzothiazole from sulfur was made by the method described above. The results of measurements of the activity of the mercaptobenzothiazole separated from the sulfur are given in Table 2.

The activity of the mercaptobenzothiazole separated from the fusion mixtures, solutions, and vulcanized rubbers and the original sulfur, was determined by means of an end-window counter tube. The background of the counter consisted of 13–15 counts per minute. The activity of the original elemental sulfur was 700–1000 counts per minute. The quantities of sulfur and mercaptobenzothiazole were taken as 2:1, i.e., the proportions of the accelerator and the sulfur were those current in practice.

TABLE 2
EXCHANGE REACTION BETWEEN MERCAPTOBENZOTHAZOLE AND RADIOACTIVE
SULFUR DURING THE PROCESS OF VULCANIZATION OF RUBBER

No. of experiments	Time (min.)	Temp. (°C)	Exchange (%)
1	15	145°	3
2	30	145°	4
3	60	145°	8
4	120	145°	13
5	180	145°	16
6	15	150°	6
7	30	150°	13
8	60	150°	24

It is evident from the experimental data given in the tables that at temperatures of 145°, 150° and 154° an intense exchange of sulfur atoms takes place between mercaptobenzothiazole and the sulfur in the fusion mixtures. No exchange was observed at 100° and below (the mixtures did not melt). The sulfur atoms also exchanged in the presence of rubber under the conditions of its vulcanization⁶.

In a well defined way, the resulting data demonstrated the presence of an intense chemical interaction between sulfur and mercaptobenzothiazole, both in fusion mixtures and in rubber mixtures at temperatures corresponding to those of vulcanization. A similar interaction is possible only during the formation of some intermediate combination between elemental sulfur and mercaptobenzothiazole (or their decomposition products) under the conditions of the experiments.

The mechanism of the exchange reaction between sulfur and mercaptobenzothiazole is still not clear. In the first place, for a judgment of the mechanism of this reaction, the position of the exchanging sulfur atom of mercaptobenzothiazole must be identified. If, as we assume, the sulfhydryl sulfur atom exchanges, then the exchange reaction may proceed by different routes, for example, by the intermediate formation of di- or polysulfide compounds, followed by rearrangement; by the shift of a hydrogen atom from sulfur to nitrogen, followed by the exchange of sulfur in the C=S bond; etc. In the same manner,

the different assumed mechanisms may be less probable, from our point of view, than the exchange of sulfur which occurs in the ring.

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- ⁶ Some retardation of the exchange is accounted for by a decrease of the concentration of the reactants, and retardation also takes place in proportion to the reaction between sulfur and rubber. We observed a similar retardation of the exchange reaction in a study of the reaction of sulfur and mercaptobenzothiazole in a cumene solution for 30-60 minutes at 148° C.

THE QUANTITATIVE ANALYSIS OF RUBBER CHEMICALS. I.*

WALTER SCHEELE AND CHRISTA GENSCH

KAUTSCHUK-INSTITUT, TECHNISCHE HOCHSCHULE, HANNOVER, GERMANY

STATEMENT OF THE PROBLEM

Studies of the reactions occurring during mastication and vulcanization of rubber must be regarded as still far from completed despite the many valuable experimental contributions. Although many theories have been developed on the mechanism of the processes to be discussed here, either based on the results of direct studies of the chemical processes or on the results of indirect physico-technological methods, one still has the impression that a thorough interpretation¹ of all the relationships is not possible at present. Mastication and vulcanization are undoubtedly very difficult problems which are chosen by the experimenter mainly because of their importance.

It is convenient to distinguish between those studies that deal with the elucidation of the reactions of the molecular chains of rubber during mastication, cyclization, and vulcanization, and those that deal with the performance of all the compounds which influence the course of these processes. At present we are interested in the second of these studies. In order to undertake the experimental work, it seemed to be desirable to have analytical methods by which we would be able to determine quantitatively the smallest amounts of accelerators, age resistors and, as well, the decomposition products of various of the rubber chemicals in question. We feel that the development of these methods is absolutely necessary for scientific studies of the kind mentioned and also desirable for the industrial laboratory. Many procedures for the analysis of rubber compounding ingredients, especially of vulcanization accelerators and age resistors, have been published; most of these, however, are for qualitative identification only². Besides precipitation and color reactions, physico-chemical methods are of considerable importance. Spectroscopic investigations of all kinds, and especially the characterization of substances by their ultrared, ultraviolet, and infrared spectra have been widely applied. Work on the application of polarography has become known. Chromatographic analysis has been put to use with marked success to separate compounds of interest and then to identify them by characteristic reactions.

Based on the idea that auxiliary rubber chemicals are advantageously removed from a vulcanizate by extraction with a suitable organic solvent, e.g., acetone, we were interested primarily in those procedures which would enable us to analyze quantitatively in the original extract itself. This would simplify considerably, though not eliminate, all of a number of working steps.

Potentiometric titration³ and especially conductometric titration⁴ appeared applicable because of the very high reactivity of the materials to be determined and also because of the possibility of studying the course of the reactions from

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the change in conductivity. Furthermore, these methods are also practical for use with colored solutions, in cases where the use of indicators is in most cases very much restricted.

This paper deals with the quantitative determination of several accelerators of industrial importance by the application of conductometric methods. However, it is concerned only with the determination of pure compounds and of mixtures of some of them.

CONDUCTOMETRIC TITRATION OF DITHIOCARBAMATES¹

TITRATION OF DITHIOCARBAMATES WITH ACID

It is well known that carbamates as well as dithiocarbamates undergo cleavage with acids. Dithiocarbamates form dithiocarbamic acid, which in turn decomposes into carbon disulfide and the respective amine. With zinc diethyl-

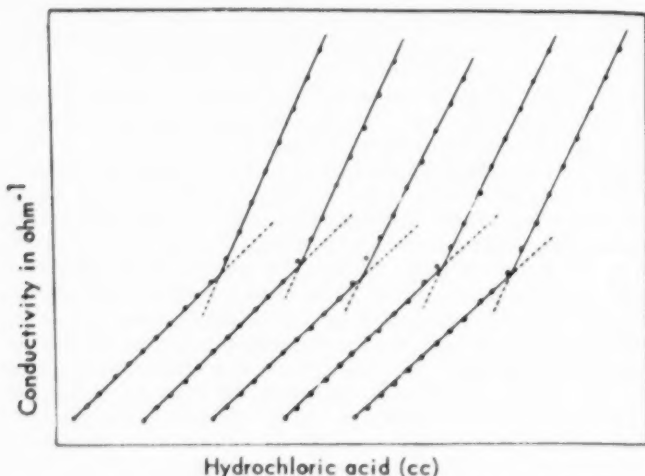


Fig. 1.—Conductometric titration of 1.81 mg. zinc diethyldithiocarbamate with hydrochloric acid.

dithiocarbamate or cyclohexylethylammonium cyclohexylethyldithiocarbamate the following reactions occur:

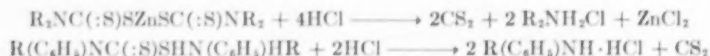


Figure 1 gives conductometric titration curves which are obtained by adding hydrochloric acid in portions to check samples of a solution of a dithiocarbamate and by measuring the conductivity after the addition of each portion of acid. As long as any dithiocarbamate remains in the conductivity cell, the conductivity increases moderately in linear fashion, because of the increasing amount of acid anions and ammonium ions of the respective bases. After all the dithiocarbamate has been used up, excess acid appears and the conductivity increases considerably faster because of the rapidly migrating hydrogen ions. The amount of acid of known concentration which has been consumed up to the

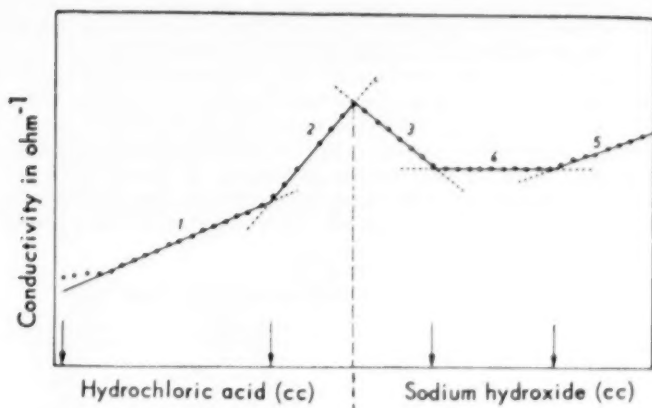


FIG. 2.—Conductometric titration of a zinc carbamate with hydrochloric acid and subsequently with sodium hydroxide.

TABLE I
TITRATION OF ZINC DIETHYLDITHIOCARBAMATE WITH ACID

Amount of carbamate (mg.)	Amount of 0.1 or 0.01 N acid consumed (cc.)	Theoretical amount of 0.1 or 0.01 N acid consumed (cc.)	Deviation from theory (%)
36.2	4.16	4.00	+4.0
	4.06	4.00	+1.5
	4.20	4.00	+5.0
	4.16	4.00	+3.0
	4.16	4.00	+4.0
	Deviation of mean value		+3.75
18.1	2.14	2.00	+7.0
	2.04	2.00	+2.0
	2.12	2.00	+6.0
	2.20	2.00	+10.0
	Deviation of mean value		+6.25
9.05	1.01	1.00	+1.00
	1.01	1.00	+1.00
	1.00	1.00	0.00
	Deviation of mean value		+0.7
3.62	4.00	4.00	0.0
	4.00	4.00	0.0
	3.98	4.00	-0.5
	Deviation of mean value		-0.17
1.81	2.12	2.00	+6.0
	2.38	2.00	+19.0
	2.04	2.00	+2.0
	2.24	2.00	+12.0
	2.20	2.00	+10.0
	Deviation of mean value		+10.0

intersection of each pair of two lines can be determined on the abscissa and corresponds to the amount of dithiocarbamate in the conductivity cell.

In the case of a zinc dithiocarbamate the simultaneous titration of zinc is theoretically possible (see Figure 2). Along the lines 1 and 2 the cleavage of dithiocarbamate occurs as indicated above, and along the lines 3, 4 and 5 zinc is subsequently titrated with NaOH. At first, excess acid is used up (line 3); the conductivity therefore decreases in proportion to the amount of added base. After this zinc is precipitated as hydroxide and the conductivity stays practically constant (line 4). When all the zinc is precipitated, the conduc-

TABLE II
TITRATION OF ZINC DIBUTYLDITHIOCARBAMATE WITH ACID

Amount of carbamate (mg.)	Amount of acid consumed (cc.)	Theoretical amount of acid (cc.)	Deviation from theory (%)
47.4	3.84	4.00	-4.0
	3.90	4.00	-2.5
	3.94	4.00	-1.5
	Deviation of mean value		-2.7
23.7	1.84	2.00	-8.0
	2.02	2.00	+1.0
	1.84	2.00	-8.0
	1.90	2.00	-5.0
	2.04	2.00	+2.0
	Deviation of mean value		-3.6
11.85	1.10	1.00	+10.0
	1.08	1.00	+8.0
	1.08	1.00	+8.0
	1.08	1.00	+8.0
	Deviation of mean value		+8.5
4.74	4.00	4.00	0.0
	3.96	4.00	-1.0
	3.96	4.00	-1.0
	Deviation of mean value		-0.67
2.37	2.02	2.00	+1.0
	2.00	2.00	0.0
	Deviation of mean value		+0.5

tivity increases again because now the rapidly migrating hydroxyl ions are present in the solution (line 5). We found, however, that the determination of zinc by this method is not accurate enough. The ammonium salts which form along line 1 seem to interfere and during the titration with NaOH along lines 4 and 5 the bases are regenerated, causing the intersection of 4 and 5 to become indefinite and thereby inducing errors. However, this titration has certain advantages even though it does not give accurate results. Thus, if only a zinc dithiocarbamate is present, the projections of lines 1 and 4 have to be in the proportion of 2:1. If this should not be the case, and the proportion is 3:1 for example, it may be concluded that besides, a second dithiocarbamate is present⁶ in addition to the zinc dithiocarbamate.

The results of our studies on the analysis of dithiocarbamates are given in Tables I to III.

From these tables it is evident that as small an amount as 4.5 mg. of sodium diethyldithiocarbamate is still easily titrated. In this case the mean error of the titration values is -3.6 per cent. As little as 2.37 mg. of zinc dibutyldithiocarbamate was determined with an error of +0.5 per cent and 3.62 mg. of zinc diethyldithiocarbamate with a mean error of -0.17 per cent. Table III shows that the deviations increase with decreasing amounts. When titrating 1.81 mg. of zinc diethyldithiocarbamate, the error was as high as +10 per cent.

TABLE III

TITRATION OF SODIUM DIETHYLDITHIOCARBAMATE* WITH ACID

Amount of carbamate (mg.)	Amount of 0.1 N acid used (cc.)	Theoretical amount of acid (cc.)	Deviation from theory (%)
67.59	6.00	6.00	0.0
45.06	3.92	4.00	-2.0
	4.02	4.00	+0.5
	3.96	4.00	-1.0
	4.00	4.00	0.0
	Deviation of mean value		-0.63
22.53	1.98	2.00	-1.00
	1.98	2.00	-1.00
	1.96	2.00	-2.00
	Deviation of mean value		-1.35
11.25	1.00	1.00	0.0
	0.99	1.00	-1.0
	1.00	1.00	0.0
	Deviation of mean value		-0.3
4.5	3.96	4.00	-1.0
	3.76	4.00	-6.0
	3.98	4.00	-0.5
	3.72	4.00	-7.0
	Deviation of mean value		-3.6

* In the form $(C_2H_5)_2NC(=S)SNa \cdot 2H_2O$.

CONDUCTOMETRIC TITRATION OF DITHIOCARBAMATES WITH SILVER NITRATE

Dithiocarbamates form a number of insoluble salts which have been described in detail Gleu and Schwab⁶. In particular the heavy-metal salts of dithiocarbamic acids are distinguished by their insolubility in water. We have found that this makes possible an additional conductometric titration of dithiocarbamates, though only to a limited extent, for it was found that titration with an acid is considerably more accurate and more reliable than titration with silver nitrate. This is briefly discussed below.

When silver nitrate is added to a solution of a dithiocarbamate, a yellow silver dithiocarbamate is precipitated. A titration curve similar to those in Figure 1 is obtained. As long as silver dithiocarbamate precipitates, the con-

TABLE IV
TITRATION OF CYCLOHEXYLAMMONIUM CYCLOHEXYLDITHIOCARBAMATE
WITH SILVER NITRATE

Amount of carbamate (mg.)	Amount of AgNO ₃ consumed (cc.)	Theoretical amount AgNO ₃ (cc.)	Deviation from theory (%)
0.826	0.9	1.0	-10
	0.92		-8
	0.91		-9
1.652	0.82	1.0	-18
	1.00		0.0
	0.94		-6.0
	0.94		-6.0
3.304	0.98	1.0	-2.0
	1.00		0.0
	0.99		-1.0
33.04	1.16	1.0	+16
	1.10		+10
	1.17		+17
	1.16		+16

ductivity rises slowly and nitrate ions and dialkylammonium ions are formed in the solution. At the end of the precipitation the relatively mobile silver ions cause the titration curve to rise more steeply. Although the two lines of the titration curve form a more obtuse angle than the curves in Figure 1 (titration with acid), it is still possible to determine the end point accurately. Table IV indicates, however, that this method is subject to systematic errors. At high concentrations too much dithiocarbamate is found and at low concentrations too little. The analyses are sufficiently accurate only at medium concentrations. Since it is generally impossible to estimate the amount of dithiocarbamate, it is necessary to be very critical in evaluating the results of this method. Whenever possible, titration with acid is always preferable.

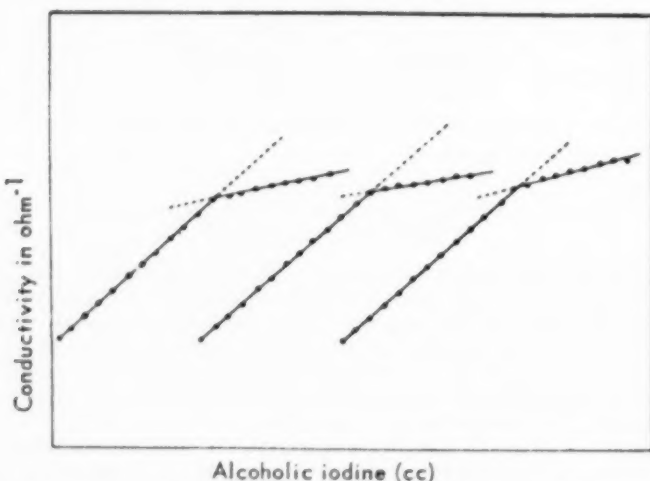


FIG. 3.—Conductometric titration of 1.185 mg. zinc dibutylthiocarbamate with alcoholic iodine solution.

CONDUCTOMETRIC TITRATION OF DITHIOCARBAMATES WITH IODINE

Dithiocarbamates are easily oxidized and form the corresponding disulfides when they are treated with common oxidizing agents. Oxidation with alcoholic iodine is especially clear-cut and also quantitative. We studied this reaction for zinc dibutyldithiocarbamate, where obviously the following reaction takes place:



TABLE V
ZINC DIBUTYLDITHIOCARBAMATE TITRATED WITH IODINE (MW 474)

Amount of carbamate (mg.)	Amount of iodine consumed (cc.)	Amount of carbamate found (mg.)	Mean deviation from calculated value	Mean deviation (%)
23.7	1.92	22.8	-1.0 mg.	-4.2
	1.90	22.5		
	1.94	23.0		
	1.90	22.5		
	Av. 1.92	Av. 22.7		
11.85	0.97	11.50	-0.15 mg.	-1.30
	0.99	11.74		
	0.99	11.74		
	Av. 0.985	Av. 11.7		
	Av. 0.985	Av. 11.7		
5.93	0.93	5.54	-0.39 mg.	-6.6
	0.93	5.54		
	Av. 0.93	Av. 5.54		
	Av. 0.93	Av. 5.54		
	Av. 0.93	Av. 5.54		
2.37	1.94	2.30	-0.06 mg.	-2.5
	1.94	2.30		
	1.96	2.32		
	Av. 1.95	Av. 2.31		
	Av. 1.95	Av. 2.31		
1.185	1.08	1.28	+0.60 mg.	+5.1
	1.04	1.23		
	1.04	1.23		
	Av. 1.05	Av. 1.25		
	Av. 1.05	Av. 1.25		
0.593	1.00	0.593	—	—
	1.00	0.593		
	Av. 1.00	Av. 0.593		
	Av. 1.00	Av. 0.593		
	Av. 1.00	Av. 0.593		

The changes in conductivity which occur during this reaction make possible a conductometric titration of the dithiocarbamate. When alcoholic iodine is added portionwise to a solution of zinc dibutyldithiocarbamate (preferably at 0° C), the conductivity rises slowly because of formation of zinc iodide. As soon as all the dithiocarbamate is oxidized to the disulfide, addition of more iodine causes scarcely any rise of conductivity. Figure 3 shows a few experimental titration curves. Here again the intersection of the two lines indicates the end point, and the amount of consumed iodine solution can be read directly. Table V gives the results of these titrations. It can be seen that as little as 0.593 mg. of carbamate in about 30 cc. is easily titrated.

ADDITIONAL METHODS FOR THE DETERMINATION OF CARBAMATES

It should be mentioned here that dithiocarbamates can also be determined colorimetrically. To accomplish this, one makes use of the copper salts, which are soluble in some organic solvents, forming yellow to brown solutions. We checked the validity of this procedure.

The dithiocarbamates are, as already mentioned, extremely susceptible to attack by oxidizing agents. These discolor the highly colored solutions of the copper dithiocarbamates by formation of the thiuram disulfide. We therefore did not use either tetrahydrofuran, or even dioxane for the colorimetric analyses, since these solvents might contain peroxides that would cause the colored solutions to fade slowly. We found that it is possible to precipitate a copper dithiocarbamate from its aqueous solution by adding small amounts of water-

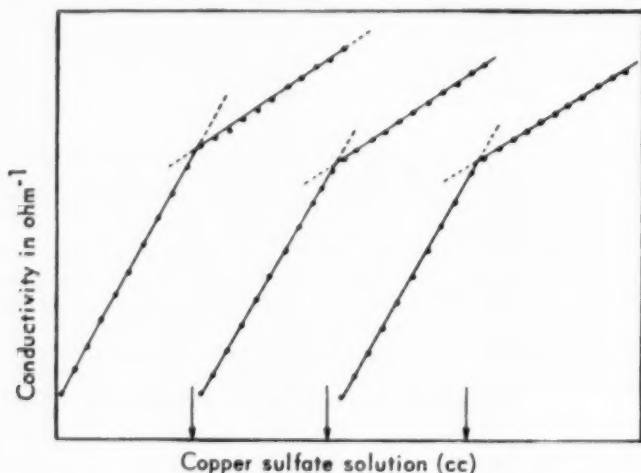


Fig. 4.—Conductometric titration of 0.60 mg. thiuram disulfide with copper sulfate in the presence of hydroquinone.

miscible organic solvents, e.g., acetone. The precipitate is filtered off and dissolved in ethyl acetate while still moist. This solution is used for colorimetric analysis. Because of the intense colors of these solutions, even minute amounts of carbamate can be determined by this method.

By the conductometric titration of dithiocarbamates, and of course also by colorimetric analysis, only the sum of carbamates present can be determined. The analysis of a mixture of carbamates would have to be supplemented by a quantitative determination of the amine hydrochlorides which are formed by cleavage. We shall discuss later how the potentiometric titration together with the conductometric titration can help us here.

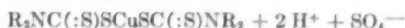
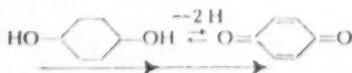
CONDUCTOMETRIC DETERMINATION OF TETRAMETHYLTHIURAM DISULFIDE

Titration with copper sulfate in the presence of hydroquinone.—Copper sulfate added to a solution of tetramethylthiuram disulfide in aqueous acetone reacts slowly with formation of a dark brown precipitate. This precipitate is the

copper salt of the corresponding dithiocarbamate. We found that this precipitation occurs considerably faster in the presence of hydroquinone. Indeed precipitation of the dithiocarbamate under these conditions is instantaneous even at low temperatures. This reaction is very well suited for a conductometric titration of a thiuram disulfide.

In Figure 4 experimental titration curves are shown. As long as unreacted thiuram disulfide is present the conductivity rises rapidly during the addition of copper sulfate solution. As soon as all the disulfide is precipitated as copper dithiocarbamate, the conductivity rises considerably more slowly or stays constant if the amount of acetone is relatively high. Here again, two lines are obtained. Their intersection gives the end point and the amount of copper sulfate consumed.

The slope of the curve can be interpreted by the assumption that hydroquinone is able to reduce the disulfide. There is always enough free dithiocarbamic acid in solution to exceed the solubility product of the copper salt; the hydroquinone produces more free dithiocarbamic acid from the disulfide, and so on. The hydroquinone obviously is transformed into quinone. This can be recognized from the green color of the solution (quinhydrone) after complete precipitation and settling of the precipitate⁷. The following reaction is probable.



The steep slope of the first part of the titration curve is caused by protons which are liberated during the reaction. The second part of the curve is less steep since it is caused by an excess of copper ions, which are much less conductive than protons.

Although too little thiuram disulfide is generally found, the method as such is reproducible. As little as 0.6 mg. of disulfide in about 30 cc. is easily determined with an accuracy of minus 2 per cent (Table VI). It is advisable to conduct the titration at moderate temperatures, e.g., at 40° C. The determination of thiuram disulfide in the presence of dithiocarbamate is described in a later section.

OTHER METHODS

It is known that tetramethylthiuram disulfide reacts with potassium cyanide⁸ according to the following equation:



Our observations indicate that this reaction is adapted to the quantitative analysis of thiuram disulfides. The following procedure is used. The solution of the tetramethylthiuram disulfide in dilute alcohol is treated with an excess of potassium cyanide and let react for a short time. The thiuram monosulfide which has been formed and which interferes considerably with the analytical determination of potassium cyanide is then extracted with benzene and the unreacted potassium cyanide is back-titrated conductometrically with silver nitrate. The thiocyanate also present in the solution does not interfere with

TABLE VI
TITRATION OF TETRAMETHYLTHIURAM DISULFIDE WITH
COPPER SULFATE (MW 240)

Amount used (mg.)	Molarity of solution	Amount of CuSO_4 consumed (cc.)	Theoretical amount of CuSO_4 (cc.)	Deviation from theory (%)
48	0.004	3.96	4.00	-1.0
		4.00	4.00	0.0
		3.98	4.00	-0.5
		Deviation of mean value		
24	0.002	1.94	2.00	-3.0
		2.00	2.00	0.0
		1.98	2.00	-1.0
		Deviation of mean value		
12	0.001	1.00	1.00	0.0
		1.00	1.00	0.0
		1.00	1.00	0.0
		Deviation of mean value		
6	0.0005	4.98	5.00	-4.0
		2.48	2.50	-8.0
		2.42	2.50	-3.2
		Deviation of mean value		
2.4	0.0002	1.98	2.00	-1.0
		1.96	2.00	-2.0
		1.97	2.00	-3.0
		Deviation of mean value		
1.2	0.0001	1.00	1.00	0.0
		0.96	1.00	-4.0
		0.98	1.00	-2.0
		Deviation of mean value		
0.6	0.00005	0.98	1.00	-2.0
		0.98	1.00	-2.0
		0.98	1.00	-2.0
		Deviation of mean value		

the titration. During all these steps it is necessary to exclude carbon dioxide, which liberates hydrocyanic acid from the potassium cyanide and thereby leads to errors. Details concerning this method will be reported later.

CONDUCTOMETRIC TITRATION OF TETRAMETHYL MONOSULFIDE WITH COPPER SULFATE

It has been shown previously that it is possible to transform thiuram disulfides (also tetrasulfides) with potassium cyanide into the corresponding monosulfides. Since it is possible to separate the monosulfides with a suitable solvent from the excess potassium cyanide and from potassium thiocyanate, the determination of the different thiuram monosulfides becomes of real interest. However, we have found that their quantitative analysis is far from simple.

Tetramethylthiuram monosulfide also reacts with copper sulfate, and, in this

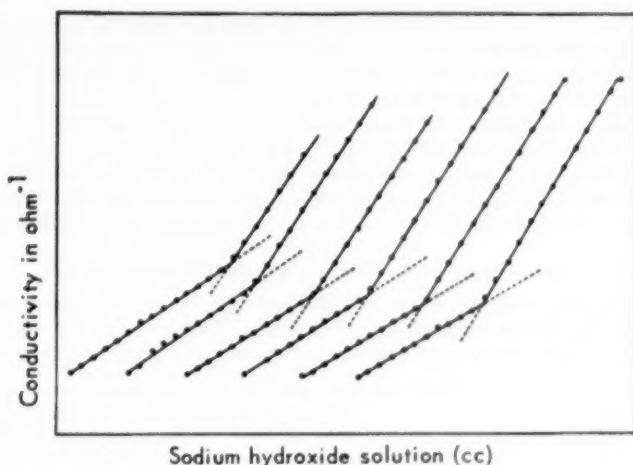


FIG. 5.—Conductometric titration of 3.345 mg. mercaptobenzothiazole with sodium hydroxide solution.

TABLE VII
TITRATION OF MERCAPTOBENZOTHAZOLE WITH
SODIUM HYDROXIDE SOLUTION

Amount used (mg.)	Amount of NaOH con- sumed (cc.)	Theoretical amount of NaOH (cc.)	Deviation from theory (%)
83.6	4.98	5.00	-0.4
	4.92	5.00	-1.6
	5.02	5.00	+0.4
	Deviation of mean value		-0.54
41.8	2.50	2.50	0.0
	2.50	2.50	0.0
	2.52	2.50	+0.8
	Deviation of mean value		+0.27
33.45	2.02	2.00	+1.0
	1.98	2.00	-1.0
	1.97	2.00	-1.5
	1.98	2.00	-1.0
	Deviation of mean value		-0.62
6.69	2.04	2.00	+2.0
	1.99	2.00	-0.5
	1.96	2.00	-2.0
	2.04	2.00	+2.0
	Deviation of mean value		+0.13
3.345	2.15	2.00	+7.5
	2.07	2.00	+3.5
	2.05	2.00	+2.5
	2.00	2.00	0.0
	2.09	2.00	+4.5
	Deviation of mean value		+3.6

case, hydroquinone apparently does not influence the reaction to any marked degree. In this case too a dark brown flocculent precipitate is formed. We investigated the applicability of this precipitation reaction to the conductometric titration of monosulfides.

The shape of the curves for these titrations is similar to that of the curves in Figure 4, but the results fluctuate considerably. It seems that the temperature at which a titration is carried out has an influence on the results. It has also been observed that monosulfide solutions undergo slow changes which influence the reaction with copper sulfate. We are now studying these conditions.

CONDUCTOMETRIC TITRATION OF MERCAPTOBENZOTHAZOLE

Titration with sodium hydroxide.—Mercaptobenzothiazole as a weak acid forms with bases the corresponding salts. The reaction can be utilized for conductometric titrations, as shown in Figure 5. If a solution of mercapto-

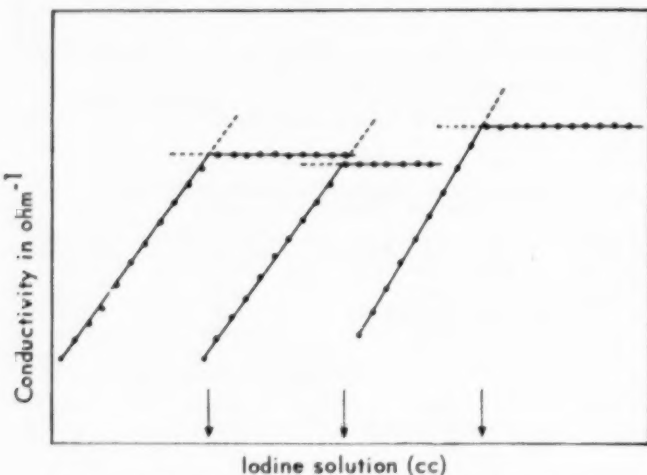
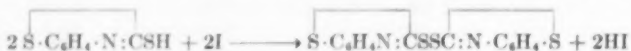


FIG. 6.—Conductometric titration of 0.835 mg. mercaptobenzothiazole with alcoholic iodine solution.

benzothiazole is titrated with standard sodium hydroxide solution, the conductivity rises at first in a linear fashion as the sodium salt of the mercaptobenzothiazole is formed. When the neutralization is complete, excess hydroxyl ions in the solution cause a much faster rise in conductivity. Here again the intersection of the two lines gives the end point of the titration. From the amount of alkali consumed the amount of mercaptobenzothiazole is calculated. The very accurate results obtained by this method are given in Table VII.

Titration with iodine solution.—Through the action of alcoholic iodine, mercaptobenzothiazole forms the disulfide in the same manner as dithiocarbamates form the respective disulfides. The following reaction occurs:



It is seen that in this case protons should be liberated and that these would cause a much faster rise of conductivity than in the case of the titration of

carbamates with iodine solution. Actually the titration diagram of Figure 6 agrees with this. As long as benzothiazolyl disulfide is being formed, the conductivity rises rapidly. It becomes practically constant as soon as an excess of iodine is present thus indicating the end of the reaction. This method of analysis of mercaptobenzothiazole is accurate, as proved by the results in Table VIII.

The addition of copper sulfate solution to a solution of mercaptobenzothiazole forms a yellow precipitate of the copper salt of mercaptobenzothiazole.

TABLE VIII
TITRATION OF MERCAPTOBENZOTHAZOLE WITH IODINE

Amount used (mg.)	Amount of iodine consumed (cc.)	Theoretical amount of iodine (cc.)	Deviation from theory (%)
33.4	4.08	4.00	+2.0
	4.08	4.00	+2.0
	3.92	4.00	-2.0
	Deviation of mean value		+0.67
16.7	2.00	2.00	0.0
	2.00	2.00	0.0
	Deviation of mean value		0.0
8.35	1.02	1.00	+2.0
	1.04	1.00	+4.0
	1.02	1.00	+2.0
	Deviation of mean value		+2.66
3.34	3.96	4.00	-4.0
	4.00	4.00	0.0
	4.00	4.00	0.0
	Deviation of mean value		-1.33
1.67	2.02	2.00	+1.0
	2.00	2.00	0.0
	2.03	2.00	+1.5
	Deviation of mean value		+0.83
0.835	1.02	1.00	+2.0
	1.00	1.00	0.0
	1.00	1.00	0.0
	Deviation of mean value		+0.67

This precipitation reaction can be utilized in two ways. If the solution of mercaptobenzothiazole is titrated directly, the titration curve is similar to those in Figure 4. As long as any copper salt is precipitated, protons are liberated, and these cause a fast rise of conductivity, while an excess of copper sulfate can be recognized by the much slower rise in conductivity. If the titration is carried out in the presence of sodium acetate, acting as a buffer, a titration curve similar to the curves in Figure 1 is obtained. The results of this titration are given in Table IX.

It can be seen that at high concentrations the analysis is subject to rather high negative deviations; however, the results become better with decreasing

amounts of mercaptobenzothiazole. The obvious inaccuracy of this method emphasizes the advantage of titrating with sodium hydroxide or alcoholic iodine.

CONDUCTOMETRIC TITRATION OF BASIC ACCELERATORS

We found that diphenylguanidine as well as *o*-tolylbiguanide is conveniently titrated by the conductometric method. The titration curves are given in Figure 7. They represent the expected neutralization curves. As long as amine hydrochlorides are formed, a moderate increase of conductivity occurs,

TABLE IX
MERCAPTOBENZOTHAZOLE TITRATED WITH CUPRIC SULFATE
IN THE PRESENCE OF SODIUM ACETATE

Amount used (mg.)	Amount of CuSO ₄ consumed (cc.)	Theoretical amount of CuSO ₄ (cc.)	Deviation from theory (%)
33.4	1.80 1.60 } 0.1 N	2.0	-15.0
	Av. 1.70		
16.7	0.90 0.98 } 0.1 N	1.0	-6.0
	Av. 0.94		
8.35	0.94 0.90 0.90 } 0.05 N	1.0	-9.0
	Av. 0.91		
3.34	1.80 2.00 2.00 } 0.1 N	2.0	-3.5
	Av. 1.93		
1.67	1.0 1.0 } 0.1 N	1.0	0.0
	Av. 1.0		

and excess acid causes the conductivity to rise considerably faster. From the intersection of the two lines the amount of acid required for the neutralization can be determined. The results⁹ are summarized in Tables X and XI.

CONDUCTOMETRIC TITRATION OF ACCELERATOR MIXTURES

CONDUCTOMETRIC TITRATION OF MERCAPTOBENZOTHAZOLE AND CARBAMATE TOGETHER

During the titration of mercaptobenzothiazole with iodine the conductivity rises considerably faster than during titration of dithiocarbamates. This led us to believe that a simultaneous titration of carbamate and mercaptobenzothiazole with iodine might be feasible. Figure 8 shows that the titration curve actually has the expected shape. Section 1 of the curve indicates the transformation of carbamate into thiuram disulfide, Section 2 the formation of

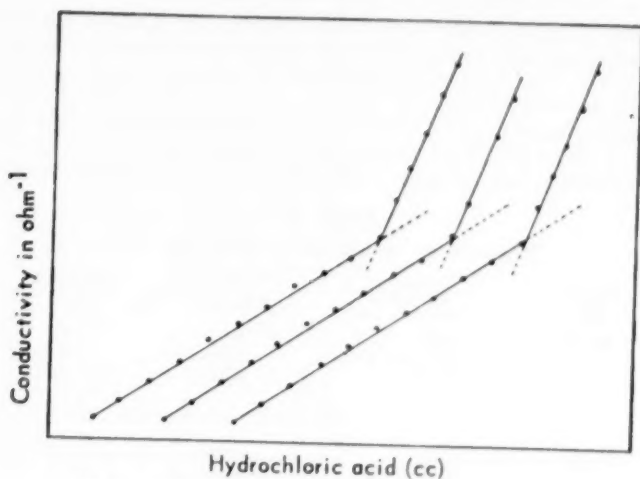


Fig. 7.—Conductometric titration of 84.44 mg. diphenylguanidine with hydrochloric acid.

TABLE X
TITRATION OF *o*-TOLYLBIGUANIDE WITH ACID

Amount used (mg.)	Amount of HCl con- sumed (cc.)	Theoretical amount of HCl (cc.)	Deviation from theory (%)
76.4	3.9	4.00	-2.5
	3.9		
	3.84		
	Deviation of mean value		-3.0
57.3	3.0	3.0	0.0
	2.98		
	3.0		
	Deviation of mean value		-0.67
			0.0
	Deviation of mean value		-0.23
38.2	2.00	2.00	0.0
	2.10		
	1.90		
	2.06		
	Deviation of mean value		+5.0
			-5.0
			+3.0
	Deviation of mean value		+0.75
19.1	1.02	1.00	+2.0
	1.00		
	1.00		
	Deviation of mean value		0.0
			0.0
	Deviation of mean value		+0.7
8.5	4.04	4.00	+1.00
	4.16		
	4.60		
	4.56		
	4.50		
	Deviation of mean value		+4.00
			+15.00
			+14.00
			+12.50
	Deviation of mean value		+9.3

benzothiazolyl disulfide (the faster rise in conductivity is due to the liberation of hydrogen ions), and Section 3 indicates the excess of iodine. The two inter-sections can be used for the determination of mercaptobenzothiazole and dithiocarbamate. This procedure, however, always leads to the detection of too much dithiocarbamate and of too little mercaptobenzothiazole, while the determination of either compound alone gives acceptable results. We assume that the hydriodic acid formed along Section 2 is able to decompose the disulfide.

TABLE XI
TITRATION OF DIPHENYLGUANIDINE WITH ACID

Amount used (mg.)	Amount of 0.1 N HCl consumed (cc.)	Theoretical amount of HCl (cc.)	Deviation from theory (%)
84.44	4.00	4.00	0.0
	4.00	4.00	0.0
	4.01	4.00	+0.25
	Deviation of mean value		+0.08
63.33	2.96	3.00	-1.33
	3.00	3.00	0.0
	3.00	3.00	0.0
	Deviation of mean value		-0.43
42.22	2.00	2.00	0.0
	2.04	2.00	+2.0
	2.00	2.00	0.0
	Deviation of mean value		+0.65
21.11	1.00	1.00	0.0
	1.00	1.00	0.0
	1.03	1.00	+3.0
	1.02	1.00	+2.0
	Deviation of mean value		+1.012
10.55	4.96	5.00	-0.8
	5.04	5.00	+0.8
	5.10	5.00	+2.0
	Deviation of mean value		+0.66
4.22	1.88	2.00	-6.0
	1.81	2.00	-9.5
	Deviation of mean value		-7.75

Therefore a larger amount of iodine is consumed than would be necessary for oxidation of the carbamate. Despite the clean-cut titration curve, a simultaneous titration of the two compounds does not give an exact result; however, another procedure is available.

The acetone-water solution of the two compounds is titrated at 40° C with acid to determine the carbamate (Sections 1 and 2). Following this titration the excess acid is back-titrated with sodium hydroxide until the solution is slightly acidic (Sections 2 and 2'). The same solution is then titrated at about 0° C with alcoholic iodine (Sections 1' and 2') to determine the mercaptobenzothiazole. This conductometric titration method has been studied with a solution of equimolecular amounts of mercaptobenzothiazole and cyclohexylethyl

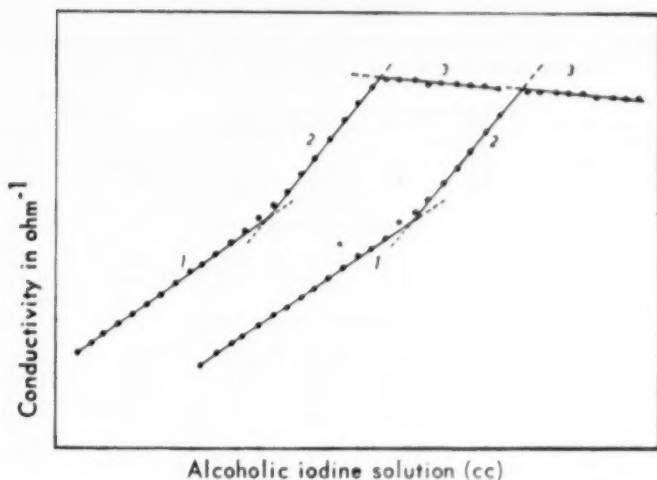


Fig. 8.—Simultaneous conductometric titration of mercaptobenzothiazole and zinc dibutyldithiocarbamate with alcoholic iodine solution.

ammonium cyclohexylethyldithiocarbamate. Table XII contains the experimental results, which evidently are quite satisfactory.

CONDUCTOMETRIC TITRATION OF DITHIOCARBAMATES AND THIURAM DISULFIDES TOGETHER

In a manner similar to the simultaneous determination of dithiocarbamate and mercaptobenzothiazole, it is possible to titrate conductometrically a solu-

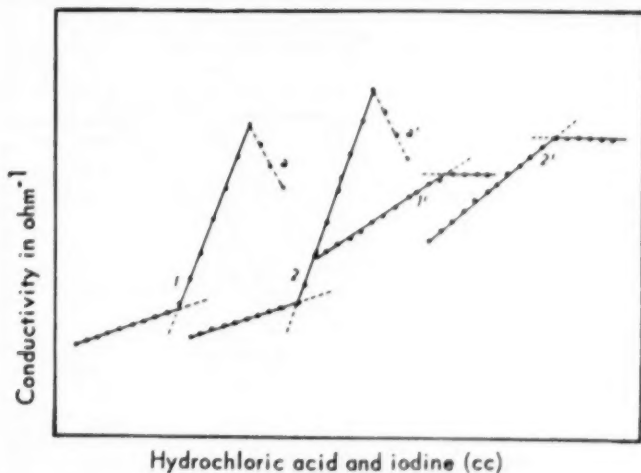


Fig. 9.—Simultaneous conductometric titration of 3.3 mg. cyclohexylethylammonium cyclohexylethyldithiocarbamate and of 1.67 mg. mercaptobenzothiazole. Curves 1 and 2: Titration of carbamate with acid. Curves 1' and 2': titration of mercaptobenzothiazole with iodine solution.

TABLE XII
TITRATION OF THE CYCLOHEXYLETHYLAMMONIUM SALT OF CYCLOHEXYLETHYL
DITHIOCARBAMATE (A) AND MERCAPTOBENZOTHAZOLE (B)

Amount used (mg.)		Theoretical cc. HCl consumed for A		Theoretical cc. Iodine consumed for B		% Deviation from theory	
A	B					A	B
33.0	16.7	2.0	2.0	2.0	2.0	0.0	0.0
		2.0	2.0	2.0	2.0	0.0	0.0
Deviation of mean value						0.0	0.0
16.5	8.35	1.00	1.0	1.0	1.0	0.0	0.0
		0.98	1.0	0.98	1.0	-2.00	-2.00
Deviation of mean value						-1.00	-1.00
3.3	1.67	1.84	2.0	2.2	2.0	-8.0	+10.0
		1.88	2.0	2.08	2.0	-6.0	+4.0
		1.88	2.0	2.04	2.0	-6.0	+2.0
		1.92	2.0	2.08	2.0	-4.0	+4.0
Deviation of mean value						-6.0	+5.0
1.65	0.835	0.90	1.0	1.0	1.0	-10.0	0.0
		0.93	1.0	1.0	1.0	-7.0	0.0
Deviation of mean value						-8.5	0.0

tion containing dithiocarbamate and thiuram disulfide. The solution of the two in acetone-water is first titrated with acid to determine the dithiocarbamate. A large part of the excess acid is then back titrated, hydroquinone is added, and the thiuram disulfide is titrated conductometrically with copper sulfate. Figure 10 shows some titration curves obtained by this method; 1, 2, and 3 are curves for the reaction of dithiocarbamate with acid, 1', 2', and 3' those for thiuram

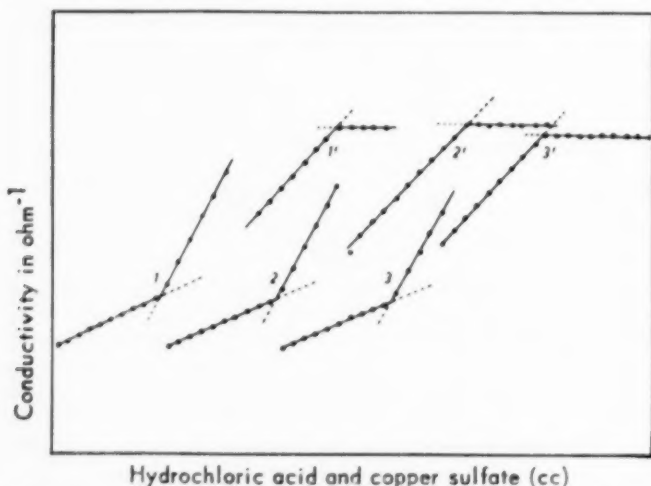


Fig. 10.—Simultaneous conductometric titration of 16.52 mg. cyclohexylethylammonium cyclohexylethylthiocarbamate and 12.00 mg. tetramethylthiuram disulfide. Curves 1, 2, and 3: titration of the carbamate with acid. Curves 1', 2', and 3': titration of the disulfide with copper sulfate.

TABLE XIII
CONDUCTOMETRIC TITRATION OF DITHIOCARBAMATE AND OF THIURAM
DISULFIDE WITH HYDROCHLORIC ACID AND COPPER
SULFATE TOGETHER

Carbamate (mg.)	Disulfide (mg.)	Cc. of HCl for carbamate	Deviation from theory (%)	Cc. of CuSO ₄ for the disulfide	Deviation from theory (%)
16.52	12.00	0.96	-4	0.88	-12
		0.96 0.1 N	-4	0.96 0.1 N	-4
		0.96	-4	0.96	-4
3.304	2.40	2.20	+1	1.92	-4
		2.00 0.01 N	0	1.91 0.001 N	-4.5
		2.00	0	1.88	-6.0
1.65	1.20	1.02	+2	1.00	0
		1.00 0.01 N	0	1.00 0.01 N	0
		1.02	+2	0.96	-4
33.04	24.0	1.92	-4	1.60	-20
		2.02	+1	1.72	-19
		1.96	-2	—	—
		1.94 0.1 N	-3	1.80 0.1 N	-10
		2.00	0	1.80	-10
		1.95	-2.5	1.74	-13
	0.6			0.92	-8
				0.94 0.005 N	-6
				0.94	-6

disulfide with copper sulfate. Table XIII lists the results of the titrations. It should be noticed that with dithiocarbamate the deviations of the results from the theoretical values are within the usual limits, while with thiuram disulfide, especially if present in relatively large amounts, the discrepancy is significant. It should be pointed out, however, that conductometric titrations tend to become more accurate with decreasing concentrations of the material being analyzed. Actually the results of the thiuram disulfide analyses are somewhat more satisfactory at lower concentrations (Table XIII), but again the results for dithiocarbamate are generally low. Adequate results for the simultaneous titration of dithiocarbamate and thiuram disulfide will be obtained if only a small amount of thiuram disulfide is present. It is also possible to analyze a solution containing dithiocarbamate and thiuram disulfide by a single titration with copper sulfate.

The titration curve in this case is similar to those in Figure 8. The addition

TABLE XIV
CONDUCTOMETRIC TITRATION OF THE CYCLOHEXYLETHYLAMMONIUM SALT OF CYCLO-
HEXYLETHYLDITHIOCARBAMIC ACID (A) AND OF TETRAMETHYLTHIURAM DISULFIDE
(B) TOGETHER

Amount used (mg.)		Amount of 0.1 N CuSO ₄ consumed		Theoretical amount of 0.1 N CuSO ₄		Deviation of mean value from theory (%)	
A	B	A	B	A	B	A	B
33.04	24.00	0.84	1.70	1.0	2.0	-3.0	-18.0
		1.02	1.70				
		0.90	1.60				
		1.10	1.54				
		Ave. 0.97	1.64				

of copper sulfate solution changes the conductivity only slightly as long as copper dithiocarbamate is being formed from soluble dithiocarbamate. However, the conductivity rises considerably faster as soon as copper dithiocarbamate is formed from thiuram disulfide, because in this case hydrogen ions are liberated. Table XIV shows some analyses of this type.

The analysis of a relatively large amount of thiuram disulfide (24 mg.) is rather inaccurate, whereas the soluble dithiocarbamate is determined from the first break in the titration curve with an error of only 3 per cent. This conductometric titration requires some experience and therefore we prefer the method used for the results in Table XIII.

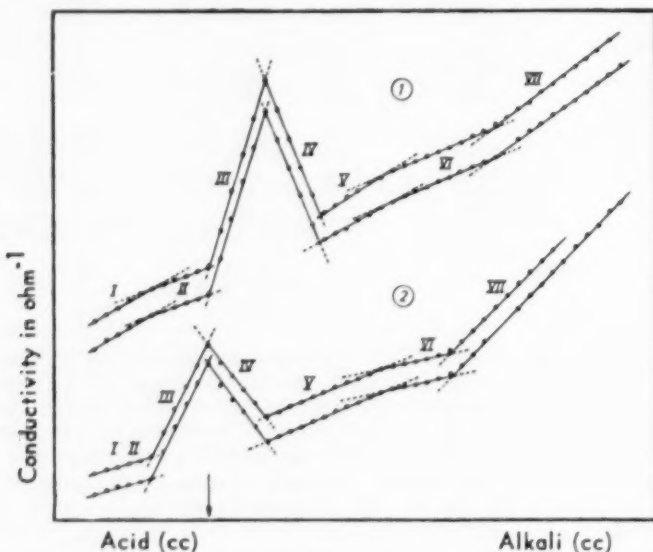


FIG. 11.—Conductometric titration of diphenylguanidine and mercaptobenzothiazole.

CONDUCTOMETRIC TITRATION OF DIPHENYLGUANIDINE AND MERCAPTOBENZOTHAZOLE TOGETHER

The use of a mixture of mercaptobenzothiazole as an accelerator is common. Therefore the simultaneous determination of the two compounds becomes of importance. If the molar concentration of diphenylguanidine is larger than that of the mercaptobenzothiazole, the conductometric titration of the solution with acid and subsequently with alkali will give the upper section (1) in Figure 11. Along line I the free diphenylguanidine and along line II the diphenylguanidine linked to mercaptobenzothiazole are transformed by the acid into diphenylguanidine hydrochloride; line III indicates the presence of an excess of titrating solution.

Hence only a single titration with acid is required for the determination of both compounds even when free diphenylguanidine is present; from line II the mercaptobenzothiazole is determined, from I and II the diphenylguanidine. Table XV (experiments 1 to 4) lists the results of such titrations. In these

TABLE XV—(Continued)

1	2		3		4		5		6		7		
	Amount used (mg.)		Theoretical amount of HCl (cc.)		Amount of HCl consumed (cc.)		Theoretical amount NaOH (cc.)		Amount of NaOH consumed (cc.)		Deviation of mean value from theory (%)		
Molar A:B	A	B	I	II	I	II	V	VI	V	VI	I	II	V
1:2 No. 5	10.55	16.71	I+II		0.50	0.1 N	1.0	0.5	0.98	0.1 N	I+II	I+II	
			0.5		0.50	I+II			1.0				
			0.1 N										
					Av. 0.50				Av. 0.99				
1:2 No. 6	4.222	6.684	I+II		1.0	0.02 N	2.0	1.0	2.24	0.02 N	I+II	I+II	
			1.0		1.0	I+II			2.30				
			0.02 N		1.0				2.12				
					Av. 1.0				Av. 2.21				
1:2 No. 7	2.111	3.342	I+II		1.0	0.01 N	2.0	1.0	1.56	0.01 N	I+II	I+II	
			1.0		1.0	I+II			1.94				
			0.91 N		0.98				2.08				
					Av. 0.993				Av. 1.86				
1:2 No. 8	1.055	1.671	I+II		0.51	0.01 N	V+VI		1.65	0.01 N	I+II	I+II	
			0.5		0.5	I+II	1.50		1.52	V+VI			
			0.01 N		0.52				1.76				
					Av. 0.51				Av. 1.64				
											-0.7		-7.0
											+2.0		+9.3

experiments the molar ratio of the compounds was 2:1. It is evident that the break in the titration curve between *I* and *II* is not very sharp at low concentrations. In such a case only diphenylguanidine is determined, and the determination of mercaptobenzothiazole must be performed by another method. If the concentrations are equivalent, however, (1, 2, and 3), the results are accurate enough, as indicated by column 7, Table XV. The amount of diphenylguanidine found from the sum of the acid consumed along lines *I* and *II* in Figure 11 checks very well with the theoretical amounts.

If the acidic solution, now containing diphenylguanidine hydrochloride and free mercaptobenzothiazole, is subsequently titrated with sodium hydroxide (Figure 11, curve *I*) the excess acid is neutralized, causing the conductivity to fall along line *IV*. Soon a sharp break occurs in the titration curve and, while the conductivity rises again, the mercaptobenzothiazole is transformed into its

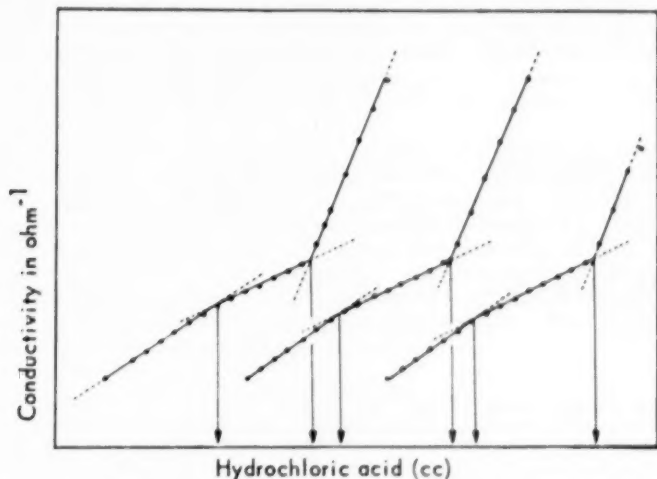


Fig. 12.—Simultaneous conductometric titration of 16.52 mg. cyclohexylammonium cyclohexylethyl-dithiocarbamate and of 10.55 mg. diphenylguanidine.

sodium salt (line *V*). Finally, the diphenylguanidine is liberated from its hydrochloride along line *VI*, and line *VII* indicates the presence of excess alkali. This leads to the conclusion that quantitative analysis of diphenylguanidine and mercaptobenzothiazole is possible by conductometric titration in acid solution with sodium hydroxide. The results are listed in Table XV, columns 5, 6, and 7. Here again it is found that the percentage deviations are within tolerable limits, as long as the concentrations are high enough (e.g., 10 mg. in 30 cc.), while the results fluctuate to a higher degree at lower concentrations. In that case the break between lines *V* and *VI* becomes so poorly defined that only the sum of diphenylguanidine and mercaptobenzothiazole can be determined.

The analysis is somewhat different if an excess of mercaptobenzothiazole is present (Experiments 5 to 8, Table XV). Here all diphenylguanidine is combined with mercaptobenzothiazole, and therefore titration with acid determines only diphenylguanidine as in sections *I* and *II* of group (2) in Figure 11. It can be seen from Table XV that the results are very accurate even at low concentrations.

During the subsequent titration with sodium hydroxide, the conditions are generally the same as in Experiments 1 to 4. However, the break between sections VI and VII is often so poorly defined that a determination of the sum of mercaptobenzothiazole and diphenylguanidine is out of the question. On the other hand, it is possible to determine mercaptobenzothiazole along section V if the concentration is not too low. In the presence of too small amounts of mercaptobenzothiazole, larger errors are likely, since in this case too the break between V and VI is usually only poorly defined. Accordingly analysis of

TABLE XVI
CONDUCTOMETRIC TITRATION OF CYCLOHEXYLETHYL-AMMONIUM SALT OF CYCLO-
HEXYLETHYLDITHIOCARBAMIC ACID (A) AND OF DIPHENYLGUANIDINE (B) TOGETHER

Amounts used (mg.)			Theoretical amount of HCl (cc.)			Amount of HCl consumed (cc.)			Deviation of mean value from theory (%)
A	B	A+B	A	B	A+B	A	B	A+B	
33.04	21.11	54.15	2.00	1.00	3.00	1.85	1.10	2.96	-2.3
						1.74	1.20	2.94	
			HCl	0.1 N		1.98	0.90	2.88	
								Av. 2.93	
16.52	10.55	27.07	1.0	0.5	1.5	0.76	0.7	1.46	-2.7
						0.96	0.5	1.46	
			HCl	0.1 N		0.96	0.5	1.46	
								Av. 1.46	
6.608	4.222	10.33	2.0	1.0	3.0			2.86	-5.3
								2.84	
			HCl	0.02 N				2.83	
								Av. 2.84	
3.304	2.111	5.415	2.0	1.0	3.0			2.86	-4.3
								2.88	
			HCl	0.01 N					
								Av. 2.87	
1.652	1.055	2.707	1.0	0.5	1.5			1.43	-5.3
								1.40	
			HCl	0.1 N					
								Av. 1.42	

mercaptobenzothiazole and diphenylguanidine together by conductometric titration is practicable within certain limits. With suitable molar concentrations of the two compounds the results are always satisfactory.

CONDUCTOMETRIC TITRATION OF BASIC ACCELERATORS IN THE PRESENCE OF CARBAMATES

The excellent conductometric titration of diphenylguanidine and *o*-tolylbiguanide makes it possible to determine quantitatively carbamates in mixtures containing them. Initially diphenylguanidine plus carbamate is determined by titrating with hydrochloric acid. If the concentrations are comparable, a titration curve like those in Figure 12 is obtained. Two breaks occur, the first one at the end point of the neutralization of the diphenylguanidine, the second one at the end of the carbamate cleavage. In principle it should be possible to

determine both compounds by a single conductometric titration with hydrochloric acid. Unfortunately, however, the first break is not sufficiently reproducible. Especially in the region of smaller concentrations it is so poorly defined that the analysis is limited to the determination of the total concentration of the two compounds. Table XVI summarizes results of this type of titration.

In the case of relatively low concentrations, where the first break in the curves of Figure 12 is not sharp anyway, it is recommended that the guanidine be determined separately by the potentiometric method. Our experiments have shown that in the presence of a carbamate this method is always adequate.

APPARATUS AND TECHNIQUES

For measuring the conductivity, two types of apparatus were used: a Type LBR conductivity tester¹⁰, and a Jander-Pfundt conductivity tester¹¹.

The LBR type of instrument works on the principle of the Wheatstone bridge and is operated by a built-in generator (1000 cycles/sec.). The measuring range covers 1 to 2,000,000 ohms. A magic eye is used as a zero-point indicator. This makes possible a fast and inertia-free regulation of the bridge minimum.

The Jander-Pfundt tester uses ordinary alternating current (50 cycles/sec.). The zero-indicator is a built-in a.c.-galvanometer. The standard resistances are 100 to 5000 ohms. Together with a voltage stabilizer, connected in series, this hookup makes possible accurate conductometric titrations.

We used standard solutions of the compounds in alcohol or acetone. Known volumes of these solutions were transferred to the conductivity cell and were diluted with aqueous acetone. Care was taken to have enough acetone present to prevent a precipitation of the materials to be analyzed. The volume of the solutions in the conductivity cell was 30 to 50 cc.

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- For the analytical chemistry of dithiocarbamates, see Gileu and Schwab, *Angew. Chem.* **62**, 320 (1950).
- Furthermore it is possible to determine zinc potentiometrically. After cleavage of the zinc dithiocarbamate with acid, one titrates with sodium hydroxide. Before and after precipitation of $Zn(OH)_2$, two clearly defined changes in conductivity occur.
- It should be pointed out that this is merely a summary of the reaction mechanism. It is likely that the copper ions play some part in the process. This has yet to be investigated.
- Von Braun and Stechele, *Ber.* **36**, 2280 (1903).
- o*-Tolylbiguanide can also be determined colorimetrically by copper sulfate, with which it forms a purple complex.
- Manufactured by the Wissenschaftlich-Technische Werkstätten, Wessobrunn/Obb.
- Manufactured by the Firma Gebr. Ruhstrat, Göttingen.

URETHAN RUBBER FROM A POLYETHER GLYCOL. PROPERTIES OF RAW POLYMER AND VULCANIZATES *

F. B. HILL, C. A. YOUNG, J. A. NELSON, AND R. G. ARNOLD

E. I. DU PONT DE NEMOURS & CO., WILMINGTON, DELAWARE

In recent years, the synthesis of polymers by reacting organic diisocyanates with compounds containing two or more active hydrogens has been studied extensively. Much of the pioneering work on the chemistry of organic polyisocyanates and their reaction products was carried out by Du Pont chemists¹. The products were fibers, elastomers, and plastomeric solids. In Great Britain, research of the Imperial Chemical Industries, Ltd., was directed toward the reaction of polyesteramides with organic diisocyanates to produce vulcanizable polymeric plasticizers, designated Vulcaprenes². In Germany, Bayer and co-workers developed the elastomer known as Vulcollan³ through their study of the reaction of polyester glycols with organic diisocyanates.

Recently, interest in isocyanate-based addition polymers has been stimulated by the commercial availability of a number of polyisocyanates. An elastomer, Chemigum-SL polyester-urethan, was announced by the Goodyear Tire & Rubber Company in 1953⁴. Both Vulcollan and Chemigum-SL are addition polymers of polyester glycols and organic diisocyanates, and both exhibit outstanding toughness and abrasion resistance relative to GR-S or natural rubber. Adiprene-B urethan rubber is a new addition polymer. It differs from other diisocyanate elastomers in that its polymeric segments are aliphatic polyethers rather than polyesters. Adiprene-B is a distinctive elastomer which combines in a single product high strength, abrasion resistance, solvent and ozone resistance, and excellent low-temperature properties.

ADIPRENE-B URETHAN RUBBER RESEMBLES COMMERCIAL DIENE HYDROCARBON POLYMERS

Raw Adiprene-B is a transparent amber-colored polymer, with a density at room temperature of 1.07 grams per cc. It is stable to chemical change during storage and shows no tendency to freeze even after prolonged exposure at -40° C. Although the viscosity of the polymer, measured in a Mooney viscometer, is considerably higher than that of GR-S 1500 or natural rubber, Adiprene-B mills smoothly and can be worked easily on large or small rubber mills.

Rotor size	Mooney viscosity			
	At 212° F		At 250° F	
	Adiprene	GR-S 1500	Adiprene	GR-S 1500
Small	60 \pm 5	30 \pm 4	55 \pm 5	23 \pm 3
Large	100 \pm 8	52 \pm 6	90 \pm 8	42 \pm 5

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 48, No. 5, pages 927-929, May 1956. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its meeting in Detroit, Michigan, May 4-6, 1955.

In contrast to the familiar hydrocarbon elastomers, Adiprene-B is a polar material. Although polar in character, it is not notably more hygroscopic than conventional elastomers:

Elastomer	Equilibrium water contents at 25° C (%)	
	R.H. 50%	R.H. 100%
Adiprene-B	0.9	2.5
Natural rubber (smoked sheet)	0.4	3.1
GR-S 1500	0.07	6.0
Neoprene Type GN	0.06	2.5

Because of its polar nature, it is soluble only in certain polar solvents and is resistant to the action of hydrocarbon solvents and oils. Solubility data for Adiprene-B are:

Solvent	Solubility (grams/100 ml. of solvent)
Tetrahydrofuran	
Plus 1.0% water ^a	5
Plus 5.0% water ^a	15
Plus 20% dimethylformamide ^a	>25
Dimethylformamide	>25

^a By volume.

The intrinsic viscosity of Adiprene-B measured in a mixture of tetrahydrofuran and dimethylformamide (87/13 by volume) is about 0.80, corresponding to a molecular weight of about 30,000.

VULCANIZATION ACCOMPLISHED BY HEATING WITH DIISOCYANATE CURING AGENT

The transformation of raw Adiprene-B to the elastic state is accomplished by heating with a diisocyanate curing agent. The structure and chemical activity of the curing agent are important since they are primary determinants governing processing safety and vulcanizate physical properties. In addition, such factors as toxicity, volatility, storage stability, and ultimate cost must be considered. Adiprene-B has been cured with a variety of organic diisocyanates representing different structural types as follows:

- Toluene-2,4-diisocyanate
- 4-Methoxy-*m*-phenylenediisocyanate
- 4,4'-Biphenyldiisocyanate
- 3,3'-Dimethoxy-4,4'-biphenyldiisocyanate
- 4,4'-Methylenediphenylisocyanate
- 4,4'-Methylenedi-*o*-tolylisocyanate
- Toluene-2,4-diisocyanate dimer
- 3,3'-Diisocyanato-4,4'-dimethylcarbanilide

Two of these compounds, 4,4'-methylenedi-*o*-tolylisocyanate and 3,3'-diisocyanato-4,4'-dimethylcarbanilide, have been studied extensively, since they represent the best compromise in properties and cost.

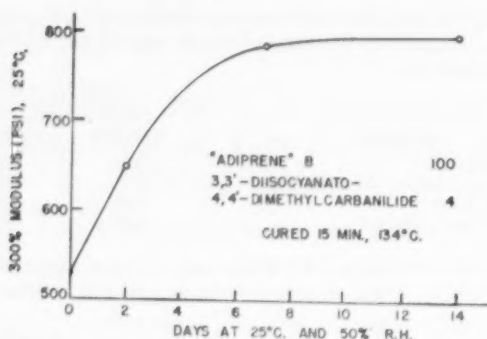


Fig. 1.—Rate of aftercure of Adiprene-B urethan rubber vulcanizate.

This urethan rubber is compounded or mixed with curing agents, fillers, and plasticizers on conventional rubber mills. Compounded stocks are shaped by calendering or extrusion and vulcanized in standard molds. Since isocyanates react with water, it is important that stocks be kept dry until they are cured. Vulcanization is effected at temperatures of 100° to 150° C. Curing times of 15 to 60 minutes at 134° C are the preferred conditions for molding.

The reaction of the isocyanate curing agent with Adiprene-B does not go to completion during the molding cycle. Vulcanization is completed by storing the product at room temperature for 7 to 14 days. The rate of the "aftercure" reaction is influenced by humidity. Figure 1 shows the effect of room temperature storage at 50 per cent relative humidity on the modulus of a vulcanizate. Other properties, such as tensile strength, compression set, and resilience also show improvement, but to a smaller degree. Therefore, our test procedure includes storage of the vulcanizate at 50 per cent relative humidity for 14 days before a final determination of properties is made.

The effect of curing agent concentration on a number of vulcanizate properties is shown in Figures 2 to 7. 3,3'-Diisocyanato-4,4'-dimethylcarbanilide

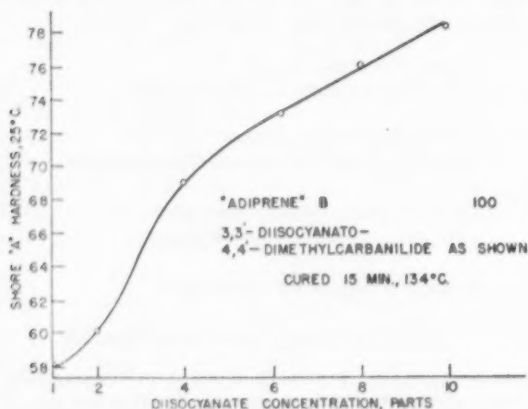


Fig. 2.—Diisocyanate concentration vs. hardness.

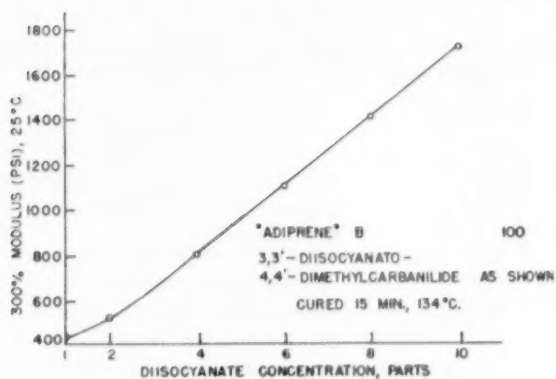


Fig. 3.—Diisocyanate concentration vs. modulus.

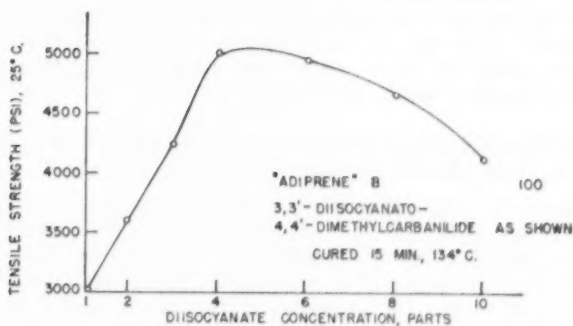


Fig. 4.—Diisocyanate concentration vs. 25° C. tensile strength.

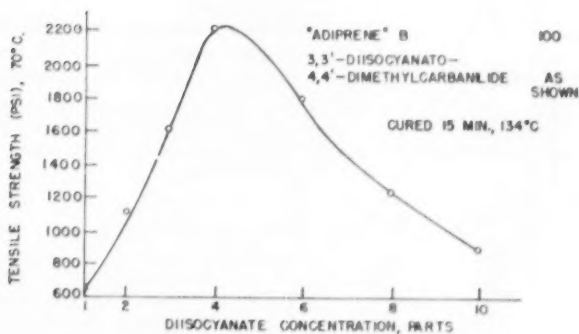


Fig. 5.—Diisocyanate concentrations vs. 70° C tensile strength.

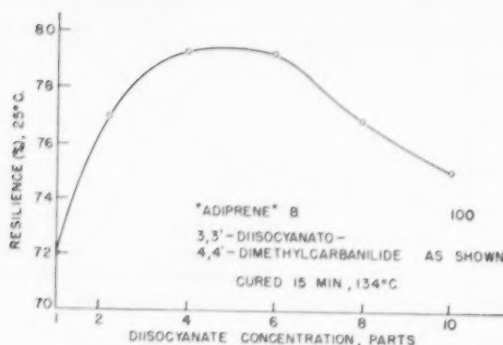


FIG. 6.—Diisocyanate concentration vs. Yezley resilience.

was used as the curing agent. The composition was cured 15 minutes at 134° C.

Figures 2 and 3 show that the hardness and modulus rise steadily as the concentration of the curing agent is increased. The tensile strength at 25° and 70° C, however, reaches a maximum at four parts of curing agent, as shown by Figures 4 and 5. The highest Yezley resilience is obtained with 4 to 6 parts of the curing agent; the lowest compression set is obtained with 6 parts, as illustrated by Figures 6 and 7, respectively.

CURED ADIPRENE-B HAS GOOD TENSILE STRENGTH, AND ABRASION AND SOLVENT RESISTANCE

Vulcanizates of Adiprene-B cured with 3,3'-diisocyanato-4,4'-dimethylcarbanilide or 4,4'-methylenedi-*o*-tolylisocyanate (Table I) have high tensile strength, exceptional abrasion resistance, and a unique combination of low-temperature flexibility and solvent resistance. The stress-strain characteristics and hardness of gum Adiprene-B vulcanizates are similar to those of a polydiene elastomer loaded with a reinforcing filler.

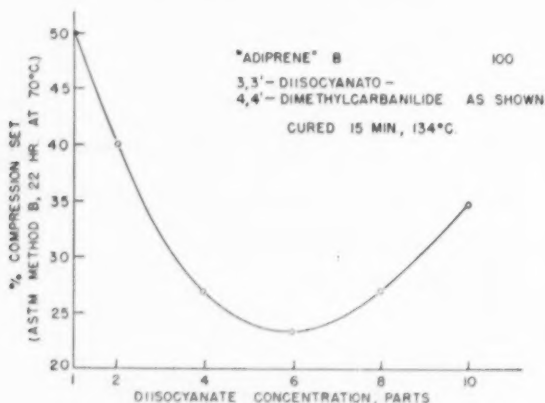


FIG. 7.—Diisocyanate concentration vs. compression set.

TABLE I
PROPERTIES OF ADIPRENE-B URETHAN RUBBER VULCANIZATES
(Test procedures: ASTM Standards, Part 6, 1952)

Adiprene-B	100	100	100	100	100	100	100	100
3,3'-Diisocyanato-4,4'-dimethylcarbanilide	4	—	—	3	—	3	4	4
4,4'-Methylenedi-o-tolylisocyanate	—	3	2.5	—	2.5	—	—	—
EPC black (Wyer)	—	—	15	15	—	—	—	—
HAF black (Phiblack-O)	—	—	—	—	15	—	—	—
Conductive channel black (Spheron-N)	—	—	—	—	—	15	—	—
Surface-esterified amorphous silica	—	—	—	—	—	—	30	—
Cab-O-Sil flame silica	—	—	—	—	—	—	—	30
Cure, 134° C (min.)	15	15	30	30	30	30	30	30
Stress-strain at 25° C in air								
Modulus at 300% (lb./sq. inch)	790	650	1400	1600	1600	1600	800	1400
Tensile strength (lb./sq. inch)	5000	4500	5200	5400	5300	5200	5000	5000
Elongation at break (%)	670	670	540	520	550	550	600	520
Stress-strain at 70° C in water								
Modulus at 300% (lb./sq. inch)	600	525	—	—	—	—	—	—
Tensile strength (lb./sq. inch)	2300	2350	—	—	—	—	—	—
Elongation at break (%)	870	1080	—	—	—	—	—	—
Shore hardness	69	63	65	68	67	73	70	78
Yerzley resilience (%)	79	76	71	73	75	73	64	60
Compression set* (%)	27	27	35	27	30	30	32	33
Bureau of Standards abrasion ^b	400-600	—	—	—	—	—	—	—
Hand tear	—	—	—	—	—	Good	Excellent	—
Volume increase, 100° C (%)								
In water, 3 days	4	4	—	—	—	—	—	—
In ASTM No. 3 oil, 7 days	32	32	—	—	—	—	—	—
Du Pont solenoid brittle temp. (° C)	< -70	< -70	—	—	—	—	—	—
Shore hardness, 14 days, -20° C	74	68	—	—	—	—	—	—

* ASTM Method B, 22 hours at 70° C.

^b ASTM Designation D394-47, Comparison Standard B.

In contrast to the polyester-urethan rubbers⁴, Adiprene-B can be reinforced with carbon blacks or silicas (Table I) to improve the hot tensile strength, abrasion resistance, and tear strength. These improvements are accompanied by a sacrifice in resilience, hardness, and compression set.

Vulcanizates having exceptional tear resistance are obtained with certain reinforcing fillers such as conductive channel blacks (Spheron-N), finely divided surface esterified amorphous silica, or Cab-O-Sil flame silica (Godfrey L. Cabot Co.). The force required both to initiate and propagate tear is high. In contrast with natural rubber vulcanizates, which owe their tear propagation resistance to "knotty" tear (a change in tear direction), Adiprene-B vulcanizates tear in a straight line.

Adiprene-B gum and silica-reinforced vulcanizates are transparent, and in

TABLE II
PROPERTIES OF AGED ADIPRENE-B URETHAN RUBBER VULCANIZATES

(Cured for 20 minutes at 134° C with 6 parts of 3,3'-diisocyanato-4,4'-dimethylcarbanilide per hundred of polymer. After aging, samples were dried, conditioned for 24 hours at 50% relative humidity, and tested at 25° C in air)

Aging conditions	Modulus at 300% (lb./sq. inch)	Tensile strength (lb./sq. inch)	Elongation (%)
Control	1100	5600	560
Water at 25° C (14 days)	1000	6000	580
Water at 70° C (7 days)	800	4200	600
Water at 100° C (1 day)	600	1900	800
Oxygen bomb (21 days at 70° C)	1100	4800	590
Dry air at 121° C (14 days)	900	3200	850

thin films are colorless. When such compositions contain oil-soluble dyes, the vulcanizates are clear and brightly colored.

The thermal, hydrolytic, and oxidative stability of Adiprene-B vulcanizates, illustrated in Table II, is similar to that observed for other urethan rubbers⁴. Vulcanizates containing carbon black show the same percentage loss of tensile properties as gum vulcanizates when subjected to such accelerated aging tests; however, the sunlight and weather resistance is improved. Gum vulcanizates possess excellent ozone resistance, and show no change in appearance after 120 hours' exposure to an atmosphere containing 100 p.p.m. of ozone.

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URETHAN RUBBER FROM A POLYETHER GLYCOL. FACTORS INFLUENCING PROCESSABILITY *

J. S. RUGG AND G. W. SCOTT

E. I. DU PONT DE NEMOURS & Co., WILMINGTON, DELAWARE

Processing studies of Adiprene-B urethan rubber have resulted in an understanding of a number of the factors required for processability. This report describes these findings in terms of:

1. Characteristics of the polymer that influence processing.
2. Principles of processing.
3. Application of these principles to some practical aspects of processing.

CONTROL OF VISCOSITY AND TEMPERATURE IS IMPORTANT IN PROCESSING

Equipment and Procedures.—Plasticity measurements were made with both the Williams parallel-plate plastometer according to ASTM Method D926-46 T¹, using onion skin paper instead of holland cloth and the Mooney viscometer according to ASTM Method D927-47 T¹, using the small rotor. Williams plasticity and recovery measurements were made at 80° C. The Mooney viscosity values reported were obtained after 4 minutes' shear unless otherwise noted. Special Mooney viscosity determinations were made using the modified equipment described. Mooney scorch determinations were made according to ASTM D1077-49 T. The temperature of the test was 121° C, unless otherwise shown. The minimum value and the time required for the viscosity to rise 10 units above the minimum were recorded.

A 14 × 30 inch two-roll rubber mill and a 6-inch Royle extruder with an 18-inch tread extruding head were used extensively throughout this work. Extrusions were run at a screw speed of 18 r.p.m. with a head temperature of 90° C and barrel and screw temperature of 20 to 25° C.

The natural rubber used for all comparisons was smoked sheet. All polymers used in plasticity comparisons were milled 15 minutes on a 6 × 12 inch mill having 15° C water circulating through the rolls.

Viscosity and Plasticity.—Mooney viscosity and Williams plasticity tests are widely used to estimate the ability of elastomers to flow and retain shapes. These properties of Adiprene-B are compared with natural rubber and GR-S 1500:

	Adiprene -B	Smoked sheet	GR-S 1500
Mooney viscosity (MS-4/100° C)	65	25	30
Williams plasticity and recovery at 80° C	390-55	160-50	130-87

Examination of these data might lead to the conclusion that Adiprene-B is very difficult to process because of its high Mooney viscosity and Williams plas-

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ticity. Actually, this is not true, since Adiprene-B bands readily on a mill and shows smoothness comparable with natural rubber.

Thermoplasticity.—Adiprene-B does not break down during milling under conditions usually used to break down other elastomers. It softens but undergoes no permanent change in plasticity or Mooney viscosity. The high viscosity of the polymer causes rapid heat generation during milling, which in turn produces rapid softening and smooth-out on the mill. The ease of milling suggests that the polymer is thermoplastic. The influence of temperature on the flow characteristics of compounded Adiprene-B is shown in Figure 1.

Adiprene-B is very thermoplastic between 80° and 100° C, but at higher temperatures, up to 121° C, it is relatively nonthermoplastic. Above 121° C a pronounced change in apparent viscosity and plasticity occurs, suggesting a change in flow characteristics. Natural rubber is relatively nonthermoplastic in the temperature range studied. Adiprene-B and natural rubber are similar

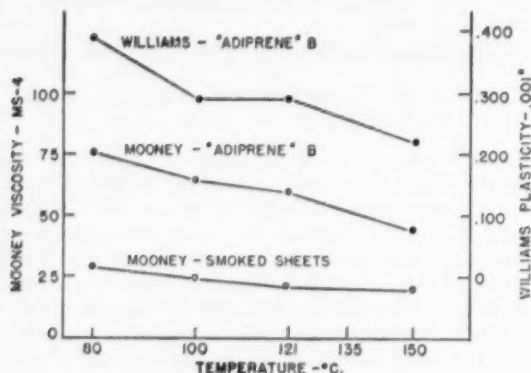


FIG. 1.—Temperature vs. plasticity and viscosity.

in their response to temperature within the temperature range normally encountered during processing (100° to 121° C), and they behave similarly during milling.

Investigation of the change in viscosity above 121° C revealed that this correlates with observed differences during milling. The optimum processing temperature range for compounds of Adiprene-B is 100° to 121° C. Higher temperatures produce a very marked deterioration in appearance and handling characteristics. During milling at temperatures within the optimum range a very smooth plastic sheet is obtained, whereas above 121° C the stock becomes rough, granular, and discontinuous. This effect is reversible and appears to depend on temperature. Return to a lower stock temperature brings back a smooth plastic sheet. The temperature at which this occurs is called the apparent transition point.

Apparent Transition Point.—The influence of temperature on this transition point was studied by measuring Mooney viscosity as the sample temperature increased continuously from 70° to 150° C. It was postulated that when the temperature rose to the transition point, the polymer would crumble and tear around the rotor, which in turn should cause the slope of the temperature-viscosity curve to decrease markedly. The break point in the curve is believed

to be indicative of the transition. This test is run using a small rotor and a starting temperature of 70° C. The test-specimen is placed in the machine and readings are taken until a constant viscosity is obtained. Then, with the machine running, the platen temperature is increased to 175° C. As the specimen temperature rises, viscosity readings are recorded at each 5° C rise in sample temperature, measured by a thermocouple imbedded in the specimen. The data are shown in Figure 2 for a gum stock and one plasticized with a liquid copolymer of butadiene and acrylonitrile.

These data confirm the hypothesis by the presence of a definite break in the temperature-viscosity curve which correlates with the temperature at which the transition is observed during milling.

The presence of the plasticizer increases the transition temperature from about 120° C in the gum stock to about 150° C. A transition temperature

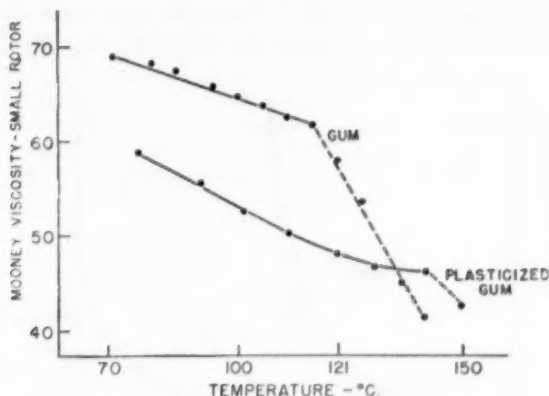


Fig. 2.—Transition vs. temperature.

above normal operating temperatures is necessary to ensure smooth trouble-free processing. A more complete study of this phenomenon is continuing, using the Mooney viscometer.

Thixotropy.—Processing observations indicate that Adiprene-B shows a different response to temperature under shear than it does in a static state. It appears to be less plastic under static conditions than under dynamic conditions—compounds flow better during extrusion than they do in a relatively static state, as molding. In addition, better molding is often obtained at a low temperature, e.g., 90° to 121° C, than at higher temperatures. This suggests that Adiprene-B is thixotropic, and its flow characteristics change with rate of shear.

Thixotropy of liquids is easily identified by viscosity tests at increasing and decreasing rates of shear, using an instrument such as the Brookfield viscometer. Methods of measuring thixotropy in solid polymers are not common. A method was devised to measure the Mooney viscosity at various rates of shear by using a machine having variable rotor speeds similar to those reported by Decker and Roth². In this modified machine, as the rotor speed increases the rate of shear relative to the die surface also increases.

By analogy with the flow curve of a thixotropic fluid, curves of viscosity versus increasing and decreasing shear rate for a thixotropic solid should be

displaced and have the appearance of a hysteresis loop with the curve for decreasing speed showing lower viscosity. Experiments were made with Adiprene-B and other elastomers, using the small rotor at 100° C starting at 0.1 r.p.m. When a constant-viscosity reading was obtained, the speed was increased to the next increment and held until the reading again became constant. This procedure was continued until a maximum speed of 20 r.p.m. was reached, after which the speed was reduced in a similar stepwise fashion until the slowest speed was reached. The speeds used were 0.1, 0.5, 1.0, 2.0, 4.0, 10, and 20 r.p.m.

The results of a comparison of milled smoked sheet and Adiprene-B using this procedure are shown in Figure 3.

The curves of viscosity for increasing and decreasing rotor speed are of the same general nature but widely separated for Adiprene-B and close together for natural rubber. Both elastomers show a characteristic plastic flow curve, but Adiprene-B has a higher yield point. These data indicate that Adiprene-B is more thixotropic than natural rubber. Practically, this means that processing speed affects both polymers similarly, but Adiprene-B is more viscous at all

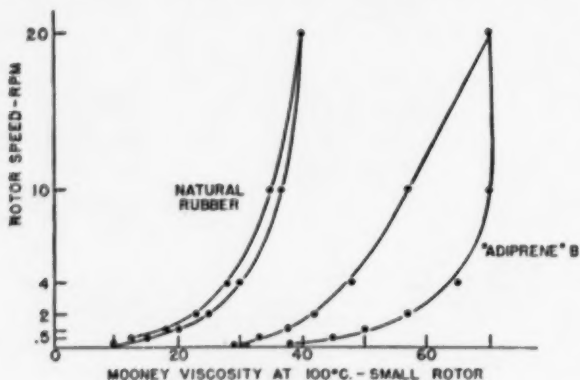


Fig. 3.—Mooney viscosity vs. rotor speed.

speeds, and continuous working reduces its apparent viscosity and tends to improve processing. The viscosity of Adiprene-B at the lowest speed is higher than the viscosity of natural rubber at the highest speed tested.

Nerve.—Recovery from deformation, commonly called nerve, is an important indicator for processing smoothness and dimensional stability of processed compounds. Attempts to judge nerve by Williams recovery led to a conclusion inconsistent with experience. Conventional Williams recovery values, at 100° to 121° C, are high, yet in actual processing at these temperatures, stock shrinkage and smoothness are at least equal to other elastomers. It is believed that the poor correlation of Williams recovery data with processing experience is due to the stiffness of Adiprene-B which resists compression of the pellet during the standard Williams test. A specimen compressed only slightly could be expected to recover more fully than one compressed to a greater extent.

A test was devised which would avoid this difficulty by compressing specimens to 50 per cent deflection in ASTM compression set Method B clamps. Standard ASTM compression set pellets were cut from uncured sheets with a rotating die. The specimens were compressed for 3 minutes at the test tem-

perature, then released, and allowed to recover for 30 minutes at the test temperature. Percentage recovery was calculated by:

$$\frac{\text{Recovered height}}{\text{Original height-compressed height}} \times 100 = \% \text{ recovery}$$

A comparison of this procedure with the standard Williams recovery, using Adiprene-B and natural rubber, is as follows:

	Williams recovery (0.001 inch)		Recovery after 50% deflection (%)	
	Adiprene -B	Smoked sheet	Adiprene -B	Smoked sheet
80° C	55	50	60	48
100° C	125	12	38	49
121° C	136	0	23	33
150° C	114	0	6	9

Adiprene and natural rubber are practically equivalent in percentage recovery or nerve when tested at equal deflection. This confirms processing experience. The conventional Williams recovery value is very high for Adiprene-B and shows very little response to temperature, whereas natural rubber reaches the point of no recovery at 121° C. However, by the modified compression set test, both elastomers lose nerve as the temperature increases.

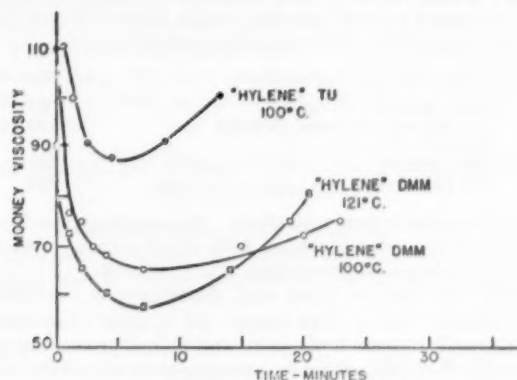


Fig. 4.—Influence of temperature on Mooney scorch.

Mooney viscosity was considered to be of more value in processing studies, since it is a dynamic test rather than a static compression test, and it was used for most testing.

Scorch.—Scorching in elastomer stocks is a change from a plastic to an elastic state brought about by a reaction of the polymer and a curing agent. Manifestation of scorch in Adiprene-B stocks is different than in other elastomers. Stocks containing Adiprene-B and curing agent increase in viscosity during scorching until they are too stiff to process. They do not become lumpy and unmillable when partially cured or scorched. Instead, they become progressively tougher and more viscous while remaining processable even in an advanced state of scorch.

Since scorching in stocks of Adiprene-B is mainly a change of viscosity and there are no complicating factors like cured lumps to contend with, the Mooney scorch test is an excellent method for estimating the scorching tendency. In addition to the usual 5- or 10-point rise, the low reading is also recorded, since it is an indication of viscosity and may be used to determine the state of scorch present in the stock at the beginning of the test.

Temperature and type of curing agent have a major influence on the rate of scorch of Adiprene-B. Figure 4 shows the influence of temperature and two curing agents on the scorch resistance of a gum stock.

Hylene-DMM (4,4'-methylenedi-*o*-tolylisocyanate) is preferred over Hylene-TU (3,3'-diisocyanato-4,4'-dimethylcarbanilide) for processing because it is less scorchy.

The slope of the curve for 121° C is steeper than the one at 100° C. This confirms actual processing experience that temperatures of 121° C and higher sharply reduce safe processing time.

PLASTICIZERS REDUCE VISCOSITY TO DESIRED LEVEL FOR PROCESSING

Processing stocks containing Adiprene-B is difficult when they become so viscous that they will not mill or extrude properly. It follows then that there is a maximum viscosity above which a stock cannot be processed.

The viscosity limit depends on the machine to be used, i.e., extruder, calender, etc., and varies according to size, design, and condition of an individual machine. Typical values found for specific equipment are:

Maximum processing viscosity	MS-4/121° C
Tread extruder (6 inch)	60
Conventional extruder (2 inch)	110
Calender (12 inch)	150
Mill (30 inch)	150
Mill (12 inch)	200

Extrusion is the most critical operation. Stocks which can be extruded can usually be processed by other methods with relative ease. Stock viscosity is influenced by two factors—compounding and scorching.

Compounding with carbon black and plasticizers is a practical means of varying stock viscosity over a wide range. As in other elastomers, the use of carbon black increases the stock viscosity and makes processing more difficult. Therefore, plasticizers are necessary in most stocks to reduce the viscosity to the desired level for processing.

A liquid butadiene-acrylonitrile copolymer, available commercially as Hycar-1312, has proved effective for plasticizing Adiprene-B. Figure 5 shows the influence of this plasticizer in combination with EPC black on the Mooney viscosity of Adiprene-B. These data show the amount of plasticizer required with a range of carbon black loadings to yield any selected stock viscosity.

Fifteen parts of plasticizer is usually ample for most types of processing. The use of larger quantities of plasticizer tends to affect vulcanizate properties adversely, as is true with other elastomers, so minimum quantities should be used.

Scorching increases stock viscosity. Therefore, a slow rate of scorch at processing temperatures is necessary to keep stock viscosity within the processable range. Scorch rate is influenced by the amount of curing agent and the compounding ingredients used. Figure 6 shows the influence of curative level

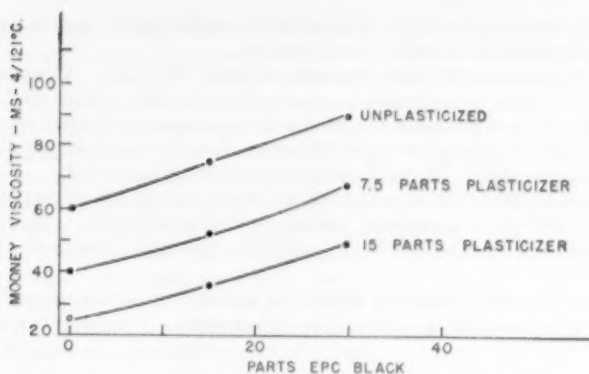


FIG. 5.—Effect of compounding on Mooney viscosity.

on the Mooney scorch rate at 121° C of a gum stock and a stock containing carbon black and plasticizer.

As would be expected, the Mooney scorch rate increases as the quantity of Hylene-DMM is increased, and use of the smallest quantity consistent with good vulcanizate properties is desirable. In most stocks, 2 to 3 parts of Hylene-DMM is optimum; however, for some uses up to 5 parts is warranted. The stock containing carbon black and plasticizer is more scorch resistant than the gum stock. This is of considerable importance in processing, since, by compounding to a lower viscosity, heat generation is reduced and this, coupled with a slower scorch rate, results in compounds capable of being processed under commercial conditions.

MAXIMUM PROCESSING TEMPERATURE SHOULD NOT EXCEED 121° C

Influence of Viscosity on Processing Temperature.—The maximum processing temperature of stocks containing Adiprene-B should not exceed 121° C. Above that temperature, stocks may be granular and semielastic because of transition.

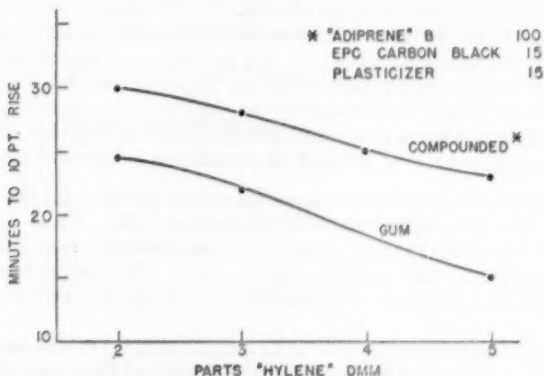


FIG. 6.—Effect of curing agent level on Mooney scorch at 121° C.

The rate of scorch is also faster than at lower temperatures, and stocks reach a maximum processable viscosity much sooner.

Processing temperature is a function of stock viscosity. Control of stock viscosity is essential to maintain processing temperature below 120° C.

Since extrusion is the most exacting of the common processing operations, a study was made of the influence of Mooney viscosity on heat generation in a 6-inch tread extruder. Figure 7 shows the results of this study.

It is evident from these data that to attain an extrusion temperature no higher than 121° C, a maximum viscosity of 50 is indicated. However, consistently better processing will be obtained if a viscosity of 30 to 40 MS-4/121° C is used.

Moisture Control.—Moisture should be avoided since it increases scorching and tends to reduce the quality of the vulcanizate. Compounded stocks ab-

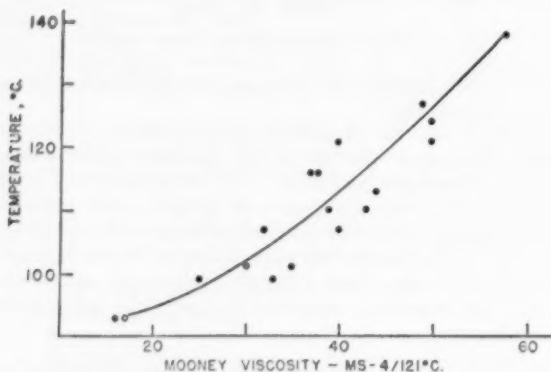


FIG. 7.—Heat generation in 6-inch extruder vs. Mooney viscosity.

sorb moisture from the air. Stocks containing curing agents should be relatively dry and provision made to keep them dry until they are cured. Adequate control of moisture is accomplished by:

1. Using dry compounding ingredients.
2. Milling the stock immediately prior to the addition of curing agent for approximately 10 minutes at 121° C. (A normal stock warm-up prior to calendaring or extrusion usually suffices to dry the stock if it has been stored between mixing and finish processing.)
3. Cooling mixed stock in air and avoiding external sources of moisture.
4. Slabbing mixed stocks as thick as possible to reduce surface area.

Bin Storage.—Stocks containing curing agent increase in viscosity during storage and become unprocessable if stored too long. Close scheduling of operations is necessary to ensure that the stock viscosity does not exceed the processable range for the operations to be used. The useful life of stocks is increased at low temperatures and humidity and when stocks are stored in thick slabs.

Six days of storage time appears to be a maximum for stocks which are to be extruded. If other processing operations, less critical than extrusion, are contemplated, the safe storage time is increased accordingly.

Compound Development.—Development of practical compounds suitable for most types of processing is accomplished by the use of the foregoing data on compounding. For example, assume that an extrudable tire-tread compound is desired. This type of stock usually requires 15 parts of EPC black for the best wear resistance, but such a stock cannot be extruded because of high viscosity. Figure 7 shows that to attain an extrusion temperature of about 110° C in a 6-inch tread extruder the Mooney viscosity MS-4/121° C should be about 40. Figure 5 indicates that a stock containing 15 parts of EPC black has a viscosity of 75, but the addition of 15 parts of plasticizer reduces the viscosity to 36 and places it in the right range for extrusion. This stock, containing 5 parts of Hylene-DMM, has a Mooney scorch rate at 121° C of 23 minutes to a 10-point rise. This is adequate in view of the fact that the stock should process at about 110° C, and at that temperature the scorch rate is even slower. This formulation has been extruded repeatedly into a smooth tread cap for experimental tire testing, using conventional equipment.

On the other hand, if this hypothetical stock is not intended for extrusion but only for calendering or molding, the stock viscosity may be higher. This reduces the amount of plasticizer required, since in these operations, processing temperatures of high viscosity stocks are more easily controlled. The limiting factor then becomes the maximum processable viscosity that allows more latitude in compounding.

SUMMARY

Adiprene-B urethan rubber is a high-viscosity thermoplastic elastomer that can be compounded and otherwise processed on conventional rubber manufacturing equipment. There are fundamental differences between Adiprene-B and the more common elastomers in processing which must be taken into consideration.

1. Processing temperatures should be less than 121° C to ensure smooth plastic flow and reduce the rate of scorching.
2. Processing temperature is proportional to Mooney viscosity, and both can be reduced by the use of plasticizers.
3. Moisture increases the rate of scorch, and it should be held to a minimum through all phases of processing.
4. Since stocks containing Adiprene-B increase in viscosity during storage, close scheduling of operations will ensure the maximum processable life.

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2-METHYL-5-VINYLPYRIDINE ELASTOMERS IN OIL-RESISTANT SERVICE *

J. F. SVETLIK, H. E. RAILSBACK, AND W. T. COOPER

RESEARCH DIVISION, PHILLIPS PETROLEUM CO., BARTLESVILLE, OKLAHOMA

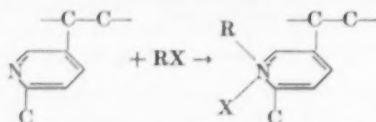
Rubbery compositions change in volume and deteriorate in physical properties when immersed in various fluids. The degree to which the dimensions and physical properties are affected depends on the immersion fluid and the temperature of service. As the temperature increases, the volume increases and the deterioration of tensile strength and elongation is accelerated.

Service temperatures have increased generally over the past few years and will probably continue to increase, paralleling developments in automotive and aircraft engineering and in other fields. At the higher temperatures there has been an increasing trend toward adoption of diester lubricants because of their stability¹. Since diesters affect rubber products more than do petroleum-base oils, rubber articles which formerly were serviceable are not capable of withstanding the deteriorating action of high temperatures and synthetic lubricants. This has necessitated the development of new materials for this type of service.

Another feature which must be considered in many applications is the low-temperature performance of the rubbery composition. Many present-day rubber products which offer the greatest oil resistance are notoriously poor in low-temperature flexibility. Freeze resistance can be improved by addition of certain plasticizers; however, the effect is fugitive because the plasticizer is extracted by the solvent with which it is in contact. Artificially introduced low-temperature flexibility is thus lost in service as the plasticizer is leached out.

A new type of rubber is required to fill the needs of present-day service. Investigations have shown that quaternized copolymers of butadiene and 2-methyl-5-vinylpyridine (MVP) and terpolymers of butadiene, acrylonitrile, and MVP meet many of the basic requirements. These elastomers give vulcanizates having excellent resistance to diesters and various other fluids and also improved low-temperature flexibility.

Oil resistance is produced by quaternizing the rubber with organic halogen compounds². This reaction is illustrated below.



The oil resistance and general physical properties are governed by the quantity of combined MVP in the elastomer and the type and quantity of quaternizing agent. Compounding is conventional with the quaternizing agent added during the mixing operation; the quaternization occurs during curing.

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EFFECT OF COMPOUNDING VARIABLES

Effect of varying quantity of quaternizing agent.—The level of quaternizing agent has been investigated in an 85/15 butadiene-MVP copolymer compounded in a typical heat-resistant recipe. Table I compares stocks containing 0, 5, 10, and 15 parts of α,α,α -trichlorotoluene per 100 parts of rubber. These data show a progressive improvement of physical properties and oil resistance as the level of quaternizing agent is raised. The quaternizing agent reduced the Mooney

TABLE I
EFFECT OF VARIABLE QUANTITIES OF QUATERNIZING
AGENT ON PHYSICAL PROPERTIES

Recipe												
Elastomer									100			
MT black									150			
Zinc oxide									5			
Stearic acid									1.5			
Plasticizer-SC									20			
Agerite Resin D									2			
Flexamine									1			
Sulfur									0.25			
Benzothiazolyl disulfide									3			
Tetramethylthiuram disulfide									2			
α,α,α -Trichlorotoluene									0, 5, 10, 15			
Cure, 45 minutes at 307° F												
α,α,α - Trichloro- toluene (propor- tion)	Com- pression set (%)	80° F				Shore hard- ness	Com- pounded Mooney (MS-14)	Volume increase (%)				
		300% modulus, (lb./ sq. in.)	Tensile strength (lb./ sq. in.)	Elonga- tion (%)	70/30 2,2,4-tri- methyl- pentane- toluene (48 hours, 158° F)			Diso- cetyl sebacate (72 hours, 300° F)				
0	6.6	770	940	525	52	25	123	117				
5	5.4	1180	1310	340	58	23	90.6	91.1				
10	6.6	1360	1670	495	63	22	69.8	52.7				
15	9.1	1210	1680	475	63	20	57.9	40.6				
Oven-aged 1 day at 212° F												
0	5	10	15	Oven-aged 7 days at 212° F			Air bomb-aged 24 hours at 260° F and 80 lb./sq. inch air					
				300% modulus (lb./ sq. in.)	Tensile strength (lb./ sq. in.)	Elonga- tion (%)	300% modulus (lb./ sq. in.)	Tensile strength (lb./ sq. in.)	Elonga- tion (%)	300% modulus (lb./ sq. in.)	Tensile strength (lb./ sq. in.)	Elonga- tion (%)
0	890	1020	510	—	1000	195	800	900	510			
5	1440	1525	395	—	1550	235	1310	1350	325			
10	1600	1860	420	—	1890	230	—	1670	290			
15	1700	1760	350	—	1510	150	—	1340	175			

value of the raw stock but increased the hardness of the vulcanizates. All the stocks had excellent retention of tensile strength after prolonged aging in a circulating air oven at 212° F and in an air bomb at 260° F and 80 pounds per square inch air pressure, particularly stocks containing 10 parts or less of quaternizing agent per 100 parts of rubber.

Effect of type of quaternizing agent.—A comparison of properties obtained with $\alpha,\alpha,\alpha,\alpha',\alpha'$ -hexachloro-*p*-xylene, α,α,α -trichlorotoluene, and chloranil is made in Table II. The data were developed in a recipe identical to that in Table I, except that the mixed antioxidant was replaced by 3 parts of BLE per 100 of rubber. The levels of the various quaternizing agents used were selected

TABLE II
COMPARISON OF QUATERNIZING AGENTS

Quaternizing agent	Compression set (%)	80° F			Scorch at 250° F (min.)	Gelman freeze point (° C)	Volume increase (%)	
Type	(Proportion)	300% modulus (lb./sq. in.)	Tensile strength (lb./sq. in.)	Elongation (%)			70/30 2,2,4-trimethylpentane-toluene (48 hours, 158° F)	Diisooctyl sebacate (72 hours, 300° F)
α, α, α -Trichlorotoluene	20	1550	1820	425	17	-64	60.4	22.8
$\alpha, \alpha, \alpha, \alpha', \alpha', \alpha'$ -Hexachloro-p-xylene	10	—	2440	190	20	-60	43.9	18.7
Chloranil	5	—	2020	220	51	-68	74.0	58.2

TABLE III
EFFECT OF CARBON BLACKS ON PHYSICAL PROPERTIES
(10 phr α,α,α -trichlorotoluene)

Black Type	Proportion	Compression set (%)	80° F			Shore hard- ness	Com- pounded Mooney (MS-1)	Volume increase (%)	
			300% modulus (lb./ sq. in.)	Tensile strength (lb./ sq. in.)	Elonga- tion (%)			70/30 2,2,4-tri- methyl- pentane- toluene (48 hours, 158° F)	Diiso- octyl sebacate (72 hours, 300° F)
MT	150	5.8	1160	1600	515	59	25	79.4	75.1
SRF	100	7.6	1820	2100	415	66	30	84.4	90.2
FEF	60	7.3	1550	2400	380	58	26	90.9	83.5

from numerous studies as the amount that gave the best balance of physical properties, with particular emphasis on swelling resistance.

$\alpha,\alpha,\alpha,\alpha',\alpha'$ -Hexachloro-*p*-xylene imparts greater oil resistance, higher modulus, lower elongation, and higher hardness than do the other quaternizing agents. Stocks containing chloranil are superior in freeze resistance but tend to be fast curing.

Pigment reinforcement.—Butadiene-MVP elastomers react normally to reinforcement by carbon blacks. The highly reinforcing blacks impart high tensile strength but, because of their greater stiffening action, must be used in moderate amounts. Soft blacks do not reinforce the compound so highly, but can be used in greater volume. The high loading reduces the volume cost of the stock and, because of the greater dilution of the rubber matrix, also reduces the degree of swelling by various immersion fluids. Typical data comparing three blacks in an 85/15 butadiene-MVP rubber quaternized with 10 parts of α,α,α -trichlorotoluene per 100 are shown in Table III.

Clay is an effective reinforcing agent in this type of rubber and yields excellent physical properties both before and after immersion in various test fluids. The relative properties obtained with clay- and black-reinforced stocks are discussed in a later section.

EFFECT OF PYRIDINE CONTENT

Investigations showed that butadiene-MVP copolymers when quaternized with halogen compounds possess better oil resistance than do similar polymers containing other vinylpyridines. Table IV compares properties of elastomers

TABLE IV
COMPARISON OF 2-METHYL-5-VINYLPYRIDINE AND
2-VINYL-5-ETHYLPYRIDINE

Elastomer	Com- pression set (%)	80° F			Shore hard- ness	Com- pounded Mooney (MS-1)	Volume increase (%)	
		300% modulus (lb./ sq. in.)	Tensile strength (lb./ sq. in.)	Elonga- tion (%)			70/30 2,2,4-tri- methyl- pentane- toluene (48 hours, 158° F)	Diiso- octyl sebacate (72 hours, 300° F)
Butadiene-MVP	4.9	1830	2130	450	67	24	45.9	26.1
Butadiene-VEP	5.8	940	1620	625	63	26	76.7	85.4

containing equal molar amounts of 2-methyl-5-vinylpyridine and 2-vinyl-5-ethyl-pyridine (VEP) compounded in the recipe of Table I, using 15 parts of α,α,α -trichlorotoluene per 100 parts of rubber. The MVP-rubber compound was significantly better than the VEP-rubber stock in stress-strain properties and oil resistance, indicating that the position of substitution on the pyridine ring is important.

In addition to the importance of the type of vinylpyridine in determining the physical properties, the butadiene-MVP ratio is also a very critical factor. The effect on physical properties of varying the MVP content of a series of rubbers has been investigated in the recipe of Table I but with 20 parts of α,α,α -trichlorotoluene per 100 parts of rubber. The test data in Table V show that the general physical properties improve with increasing MVP content, while the freeze point increases. The 75/25 butadiene-MVP rubber gives better oil resistance than does the 85/15 copolymer and still exhibits good low-tem-

TABLE V
PROPERTIES OF VARIABLE BUTADIENE-2-METHYL-5-VINYLPYRIDINE RATIO ELASTOMERS

Butadiene-MVP ratio	Com- bined MVP (%)	Com- pression set (%)	80° F			Shore hard- ness	Freeze point (° C)	Volume increase (%) (70/30) 2,2,4-tri- methyl- pentane- toluene (48 hours, 158° F)
			300% modulus (lb./ sq. in.)	Tensile strength (lb./ sq. in.)	Elonga- tion (%)			
85/15	12.4	7.9	1200	1970	520	60	-68	52.7
80/20	18.0	8.4	1310	2080	460	58	-63	37.0
75/25	20.5	8.9	1550	2070	440	59	-57	34.3
70/30	24.2	8.1	1930	2100	400	66	-48	33.6
60/40	30.7	8.2	—	1740	235	82	-38	19.7

perature flexibility. The 60/40 copolymer has poorer tensile strength and elongation than the other copolymers in the series and is much poorer in freeze resistance, but excels in oil resistance.

COMPARISON OF MVP-CONTAINING ELASTOMERS AND COMMERCIAL BUTADIENE-ACRYLONITRILE COPOLYMER CONTROLS

The foregoing discussion outlined the basic elements of compounding butadiene-MVP rubber for optimum oil resistance. Terpolymers of butadiene, acrylonitrile, and MVP react similarly and, because of the influence of the acrylonitrile, exhibit some unique properties. An investigation was made to compare the oil resistance of an 85/15 butadiene-MVP copolymer and 70/15/15 and 70/20/10 butadiene-acrylonitrile-MVP terpolymers to that of two commercial oil-resistant rubbers. The two controls are designated as A and B, and contain approximately 18 and 26 per cent combined acrylonitrile.

Each of the rubbers was compounded in black- and clay-reinforced recipes. The MVP-containing polymers were compounded with α,α,α -trichlorotoluene, $\alpha,\alpha,\alpha,\alpha',\alpha'$ -hexachloro-*p*-xylene, and chloranil. The test recipes are shown in Table VI.

For this series of compounds the change of volume and tensile strength after immersion (wet tensile) was determined in various fluids. The results are shown in a series of bar graphs.

TABLE VI
COMPOUNDING OF MVP- AND ACRYLONITRILE-CONTAINING COPOLYMERS

	Test recipes	
	100	100
Rubber	100	100
MT black	150	—
Hard clay	—	144.43
Zinc oxide	5	5
Stearic acid	1	1
Plasticizer-SC	20	20
Sulfur	0.25	0.25
Altax	3	3
Tuads	2	2
BLE	3	3
Quaternizing agent	Variable	Variable

Charge-monomer ratio	Quaternizing agent levels		Tri-chloro-toluene (proportion)	Hexa-chloro-p-xylene (proportion)	Chloranil (proportion)
	Combined monomers (%)				
	Aen*	MVP			
85/15	—	14.1	20	10	5
70/15/15	12.9	13.7	10	5	2.5
70/20/10	19.8	8.8	10	5	2.5
Control A	—	—	None	None	None
Control B	—	—	None	None	None

* Acrylonitrile.

Tensile properties of the original stocks are presented in Figure 1. The butadiene-MVP copolymer and the two terpolymers possess fairly similar tensile strength in black- and clay-loaded stocks and are appreciably better than the controls in this property.

The volume increase and wet tensile strength of specimens which were immersed for 7 days at room temperature in acetone, carbon tetrachloride, 10 per cent sulfuric acid, or 10 per cent sodium hydroxide solution are presented in

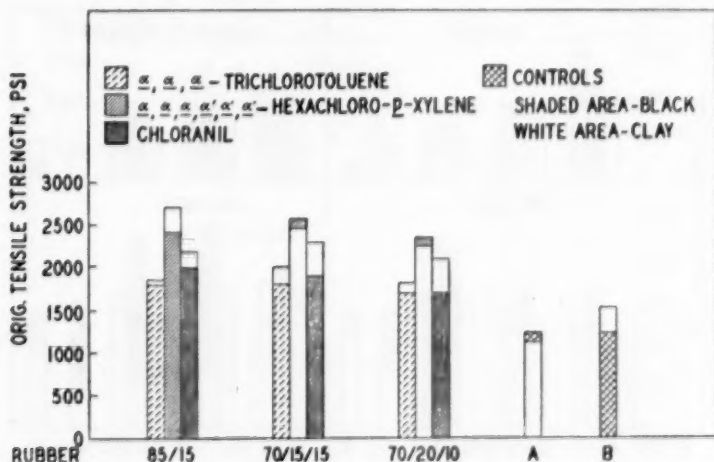


FIG. 1.—Effect of rubber, quaternizing agent, and filler on original tensile strength.

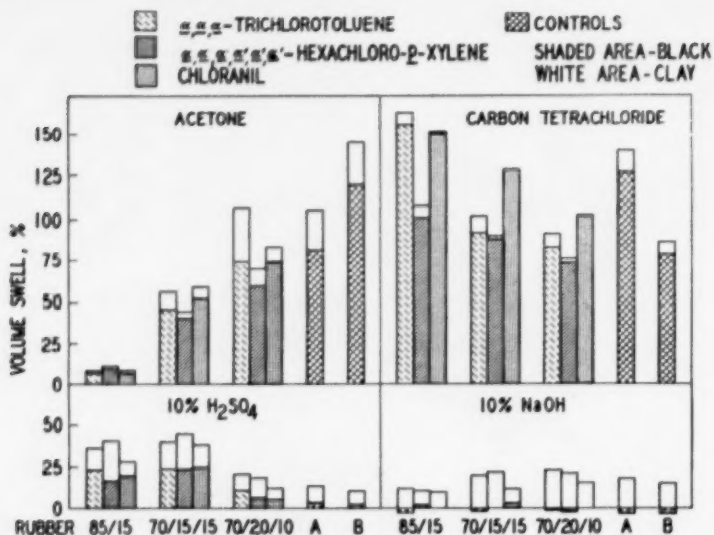


Fig. 2.—Effect of rubber, quaternizing agent, and filler on volume increase by 7-days of immersion at 80° F.

Figures 2 and 3, respectively. The butadiene-MVP copolymer is superior to the control rubbers in resistance to attack by acetone. The two terpolymers are also better than the controls, but increasing the acrylonitrile level lessens the resistance of the rubbers to acetone. In general, the black-reinforced

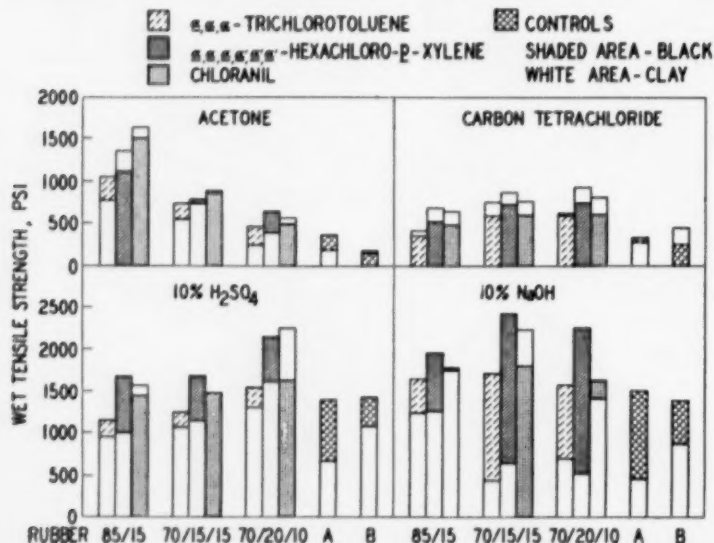


Fig. 3.—Effect of rubber, quaternizing agent, and filler on wet tensile strength by 7-days of immersion at 80° F.

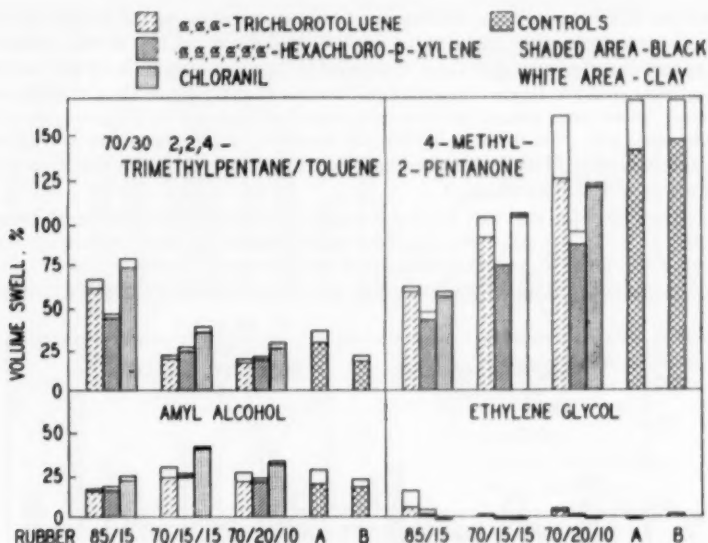


Fig. 4.—Effect of rubber, quaternizing agent, and filler on volume increase by 48-hours of immersion at 158° F.

stocks give less volume increase and equal or better retention of tensile strength than clay compounds.

All the compounds are swollen to a large degree by carbon tetrachloride; the 70/20/10 terpolymer quaternized with $\alpha,\alpha,\alpha',\alpha'$ -hexachloro-*p*-xylene is best.

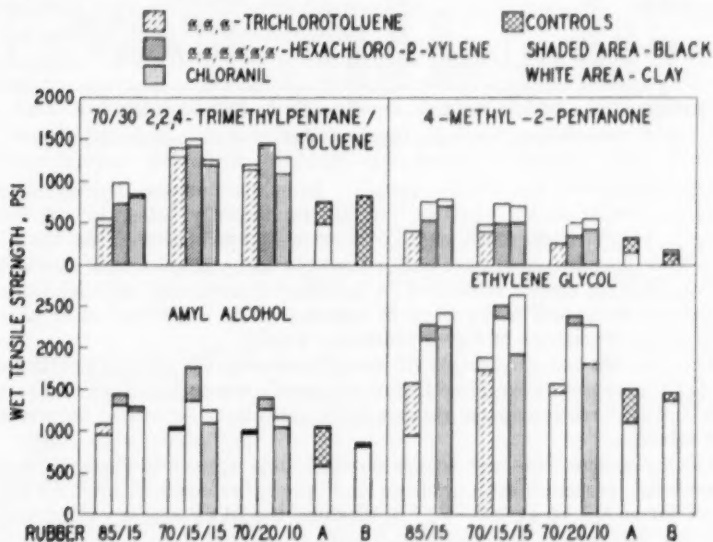


Fig. 5.—Effect of rubber, quaternizing agent, and filler on wet tensile strength by 48 hours of immersion at 158° F.

All of the MVP-containing elastomers give better retention of tensile strength than the controls after immersion in this test fluid. Clay stocks possessed better wet tensile strengths than comparable black compounds in this solvent.

Sulfuric acid swells the experimental stocks slightly more than the controls; however, these compounds are generally equal or superior to the controls in wet tensile strength. In sodium hydroxide solution, all compounds are affected to a minor degree, but again the experimental compounds are superior to the controls in wet tensile strength.

Volume increase and wet tensile strength data for stocks immersed 48 hours at 158° F in 70/30 2,2,4-trimethylpentane-toluene mixture, 4-methyl-2-pentanone, amyl alcohol, and ethyleneglycol are shown in Figures 4 and 5. In the medium aromatic fluid the 85/15 rubber gives the highest volume increase, but

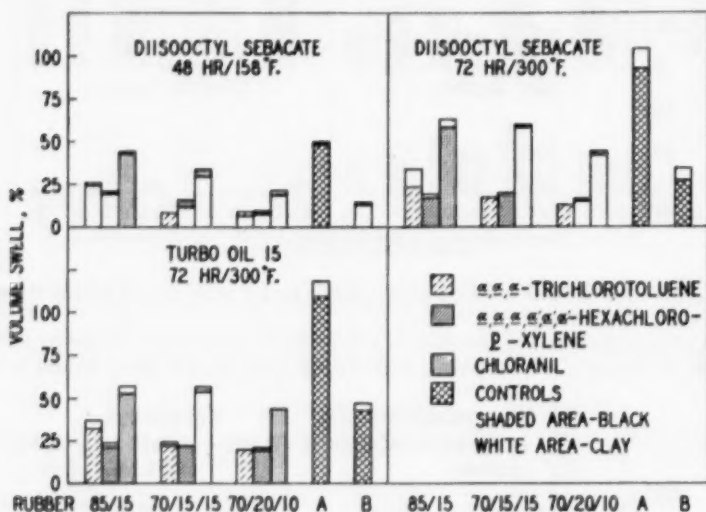


FIG. 6.—Effect of rubber, quaternizing agent, and filler on volume increase in diester oils.

exhibits satisfactory wet tensile strength. In volume increase, the terpolymers are fairly similar to the controls, but are significantly better in wet tensile strength. Clay stocks swell slightly more in this solvent than do the black compounds, but are equal to or better than the latter in wet tensile strength.

Properties of stocks immersed in 4-methyl-2-pentanone parallel those of compounds subjected to swelling in acetone. The deterioration is slightly greater with the ketone of higher molecular weight.

Amyl alcohol and ethyleneglycol do not deteriorate the rubbers significantly. The MVP compounds exhibited higher wet tensile strength and, on an average, black and clay reinforcement appears to be equivalent for stocks immersed in these solvents.

Volume increase and wet tensile strength data appear in Figures 6 and 7, respectively, for vulcanizates immersed in diisooctyl sebacate at 158° and 300° F and in Turbo Oil 15 at 300° F. In diesters, the MVP stocks exhibit only a moderate volume change; the terpolymers compounded with α,α,α -trichlorotoluene or $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -hexachloro-*p*-xylene are best in this respect and excel

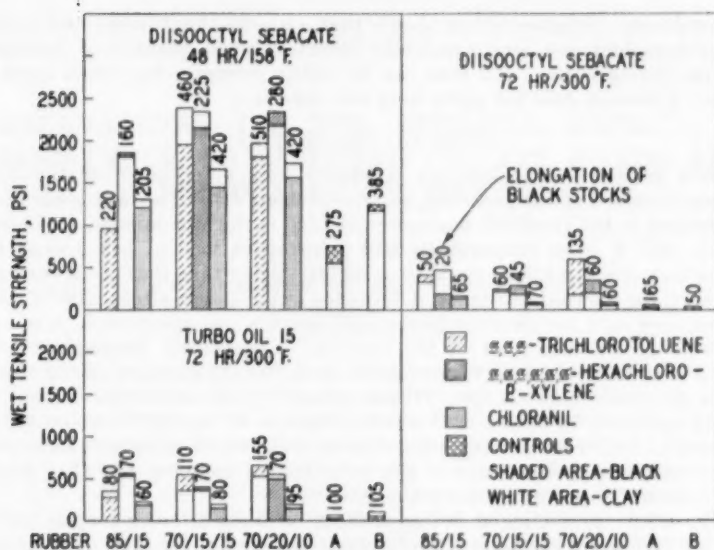


FIG. 7.—Effect of rubber, quaternizing agent, and filler on wet tensile strength.

the controls. After immersion in these solvents, all of the MVP-containing rubbers give higher tensile strengths than the controls.

In Figure 7 the elongation at break for the black-reinforced stocks is shown above each bar. The compounds exhibit relatively low elongations after immersion for 72 hours at 300° F. After immersion for 48 hours at 158° F, the elongations were satisfactory and the experimental compounds were superior to the controls in wet tensile strength.

$\alpha,\alpha,\alpha',\alpha'$ -Hexachloro-*p*-xylene imparts the greatest resistance to solvent attack in almost all of the fluids used in this series of tests. This is evident in the lower volume change and higher wet tensile strength obtained with the quaternizing agent. The chloranil-quaternized stocks possess somewhat better low-temperature flexibility. Highest elongation is obtained with α,α,α -tri-

TABLE VII
HYSTERESIS PROPERTIES OF MT BLACK-REINFORCED STOCKS

	Butadiene-MVP	Butadiene-acrylonitrile-MVP		Control	
	85/15	70/15/15	70/20/10	A	B
	α,α,α -Trichlorotoluene			No quaternizing agent	
Heat generation (ΔT° F)	107	101	94	67	74
Min. to blow-out	11	27	11	17	9
ΔT° F at blow-out	251	223	250	146	142
	$\alpha,\alpha,\alpha',\alpha'$ -Hexachloro- <i>p</i> -xylene				
Heat generation (ΔT° F)	75	73	75		
Min. to blow-out	50	> 60	> 60		
ΔT° F at blow-out	114	125	132		
	Chloranil				
Heat generation (ΔT° F)	85	85	86		
Min. to blow-out	26	> 60	17		
ΔT° F at blow-out	148	132	194		

chlorotoluene. Experience has shown that α,α,α -trichlorotoluene and $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -hexachloro-*p*-xylene apparently liberate a small quantity of hydrogen chloride during curing, and thus can be mildly corrosive to certain types of steels. Chloranil does not suffer from this deficiency.

DYNAMIC PROPERTIES

Heat generation and blowout resistance were determined for the compounds discussed in the preceding section (Table VII). The heat generation, determined in the Goodrich flexometer at 1750 cycles per minute, 0.175-inch stroke, 100° F oven temperature, and compressive load of 143 pounds per square inch, was essentially equal to or slightly higher than that of the controls. However, the blowout resistance, determined at 0.250-inch stroke, 200° F oven temperature, and compressive load of 257 pounds per square inch, was considerably better than that of the controls. Compounds quaternized with $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -hexachloro-*p*-xylene required from 50 to in excess of 60 minutes to fail in the severe blowout test. Those containing chloranil also exhibited excellent resistance to failure in this test. Failure of the MVP-rubber stocks occurred at higher temperatures than the controls, which again shows the good high-temperature performance of the experimental compounds. Clay stocks are considerably poorer in blowout resistance.

The ability to withstand flexing without breaking or crack propagation is also an important characteristic of rubber articles in dynamic applications. The flex life of an 85/15 butadiene-MVP rubber stock quaternized with 20 parts of α,α,α -trichlorotoluene per 100 of rubber was determined. The experimental stock withstood 116,000 flexures before failing, compared to 9000 flexures to failure for a GR-S-1500 compound. This test was conducted in a DeMattia flexing machine operating at 210° F and a 3-inch stroke. The remarkably good flex life is noteworthy in view of the other properties of this type of compound.

CONCLUSIONS

Butadiene-MVP copolymers and butadiene-acrylonitrile-MVP terpolymers are a new class of rubbers which can be rendered oil-resistant by reaction with organic halogen compounds during vulcanization. The rubbers respond normally to reinforcement by carbon black and are highly reinforced by mineral fillers such as clay. Oil resistance depends on MVP content of copolymers and MVP and acrylonitrile content of terpolymers. The type and quantity of quaternizing agent also regulate the properties and oil resistance of the vulcanizates.

Excellent performance of the experimental rubbers was demonstrated after immersion in ketones, amyl alcohol, ethyleneglycol, acid, caustic soda, a 70/30 2,2,4-trimethylpentane-toluene mixture, and ester solvents. The terpolymers offer better resistance to aromatic hydrocarbons. The experimental rubbers are also superior to the butadiene-acrylonitrile control compounds in contact with hot diester lubricants, giving much higher tensile strength after exposure for 72 hours at 300° F or 48 hours at 158° F.

The MVP-containing rubbers possess excellent resistance to flex crack growth. They are also considerably better than the controls in resistance to blowout under severe conditions of rapid cyclic deformation under heavy load at elevated temperatures.

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OBSERVATIONS ON THE PHYSICAL ASPECTS OF RESISTANCE TO SKIDDING ON DRY ROADS AND PARTICULARLY ON WET ROADS *

K. KNAUERHASE

PHOENIX GUMMIWERKE A.G., HAMBURG-HARBURG, GERMANY

INTRODUCTION

To ensure safety from skidding, attention has up to now been devoted to building rough surface roads, to the development of the proper vehicle construction with respect to this feature, and to the factor most directly involved, the tires. Special attention has been directed in connection with this latter phase to a much more open tread patterning and to the effect of decreasing tire inflation, both of which affect the life of the tire adversely. These steps neglected to take advantage of the physical effect of adhesion, which, without lowering the durability, now makes possible an enhanced contribution to the cohesive friction by the profile grooves which are of necessity retained to keep the weight down. The goal is, therefore, to provide the smooth surfaces of the tread pattern that come in contact with the road with the greatest possible physical gripping power, or adhesion.

After illustrating the interfacial magnitudes with the help of a vector diagram, we shall survey the laws of boundary surface adhesion. Here the great influence of the liquid involved in wet friction becomes clear and the particularly favorable interfacial tension property of water can be assessed. Since skidding can occur only at the interfaces: rubber-water, or water-road, the requirement is as follows: both the greatest possible wetting power between rubber and water, and also between water and road surface, that is, hydrophilic properties in the rubber and hydrophilic road surfaces, in order to reduce the danger of skidding. Good insurance against skidding requires hydrophilic rubber and a hydrophilic road surface, for a tire that has been developed to be nonskidding holds on a hydrophilic road surface and skids on a hydrophobic road surface. A hydrophobic tire, on the other hand, skids on any wet road.

Although considerable advances have been made with respect to safety from skidding since rubber tires were first developed for motor vehicles, with increase of speeds this problem demands our attention to a greater and greater degree. Safety from skidding can result only from the combined efforts of road and car builders, tire makers, and the chemists and physicists of all three groups.

ATTAINABLE TRACTION AND NECESSARY TRACTION

Skidding occurs when the available traction is less than that necessary between tire tread and road surface. By necessary traction is meant the adhesive friction, determined at any instant in the motion by weight, construc-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Donald J. Kitchin from *Kautschuk und Gummi*, Vol. 8, Special Issue on Tires, September 1955, pages 10-13.

tion, and driving power, which makes possible in general the forward-rolling motion of the vehicle. The necessary traction is equal to the sum of the power built into the car in the motor and the resistance to forward motion. It can, therefore, be treated as an externally applied force setting the vehicle in motion.

It is the task of the automobile builder to keep the necessary traction as low as possible. The driver too, by his manner of driving, exercises an influence on the traction necessary. By violent braking and resultant increase of the resistance to forward motion, he can make the necessary traction greater than that which is available, so that skidding ensues.

The tire maker has no control over this. For him the upper limit of the attainable traction is the decisive question. Consequently the problem of safety vs. skidding is synonymous for the tire expert with that of the attainable traction.

According to the concepts about the course of pure rolling action, the magnitude of the available traction is largely independent of the state of motion of the vehicle, so that it can be equated to the attainable traction at rest, analogous to the situation in the case of a support under compression, e.g., a pillar under a load. This device does not lead to any contradiction with experience, and is, moreover, confirmed by measurements at low speeds (about 4 km. per hour). Hence the skid resistance of a tire is given by the coefficient at rest.

The friction of two plane surfaces in contact, in our case, rubber-road, is given by Coulomb's law:

$$R = \mu \cdot P$$

where R is the frictional resistance and P is the applied pressure. The proportionality factor μ is the coefficient of friction. It is not a constant, but depends on the nature and material composition of the surfaces involved, on the temperature, on the deformability of the material, and on the boundary forces. On a wet road the surface tension forces of the water also contribute.

Without minimizing the importance of the vehicle design, the tread pattern, the roughness of the road surface, etc., as factors involved in insurance against skidding, we direct our attention here to the possibility of further increasing the skid resistance by taking advantage of the physical surface effect, i.e., the adhesion. It makes possible an enhanced contribution of the tread pattern, necessarily unchanged because of the load conditions, to the available traction, and this without reducing the life of the tire.

The problem with respect to the tire is, then, to impart to the smooth surfaces of the tread in contact with the road the greatest possible adhesion, or physical gripping power.

The magnitude of the coefficient of friction μ also depends on the properties of solid bodies, for example, the hardness. On the other hand, wetting experiments with glass or the cold welding process show the extraordinarily great influence of surface properties on the adhesion. The attraction of water to a cleaned glass surface is so great that it cannot be removed from the glass by wiping. Cold welding also illustrates the enhancement of adhesion. As soon as the clean, i.e., the true solid surfaces, free of foreign substances, come into contact, there is bonding. These effects can be of a chemical or a physical nature; it is always difficult to separate surface physics and chemistry. They differ less in actuality than in the concepts about them.

PHYSICAL INTERFACIAL MAGNITUDES

Let us now apply the known facts of surface physical phenomena, which play an important role in daily life, as in washing, in welding and soldering procedures, in flotation, etc., to the problem of the interfaces: rubber-road surface, and in particular to the boundary surfaces rubber-water, and water-road, in the case of wet friction, since this is where better safety from skidding is to be effected.

If the coefficient of friction of rubber depends on the interfacial forces of the systems involved in our case, rubber-water, and water-road, a point that will be proved in the course of this exposition, then, for good gripping of the road, the same measures need to be taken as for reducing slippage of the tires, and the freedom from skidding of a vehicle depends on the weaker of the two bonds, rubber-to-water or water-to-road. In order to illustrate and to measure the influence of the interfacial forces, the so-called inclined plane, which is so advantageous in experiments on friction, was employed (Figure 1). By

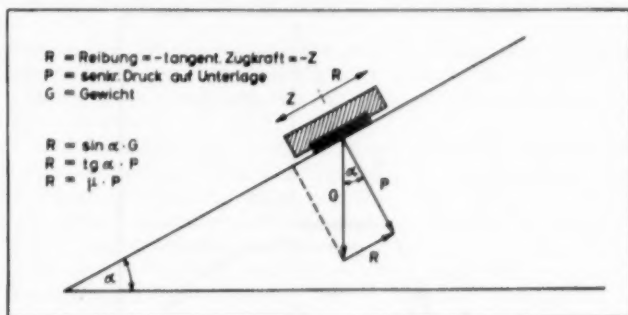


Fig. 1.—Diagram of forces for the inclined plane. R = Friction = - tangential traction = $-Z$. P = Pressure normal to surface. G = Gravity.

means of a gradual progressive increase of the angle of inclination of the sliding path, the angle α at which the rubber sample begins to slide is determined. Then the tangent of this angle is the coefficient of friction of the rubber under these experimental conditions.

The reproducibility of the results obtained in this way is very good in the range of greatest interest, from 20° to 50° , and is, in fact, $\pm 1^\circ$. Thus it is easily possible in this way to arrive at a standardization of rubber qualities.

As soon as sliding starts, the measurement changes from a static to a dynamic one. Such dynamic studies were carried out, but with another device, which gave the same order for the different types of rubber.

Now, on the basis of boundary surface physics, it is to be expected that rubber compounds of hydrophilic character will show a large sliding angle, and the experiment with the inclined plane confirms this, in that hydrophobic types show consistently very small angles for wet friction, whereas hydrophilic types give angles, for example, of 45° to 50° , and special types even attain the angle of dry friction, i.e., 53° . Thus there is the possibility of obtaining considerable safety from wet skidding by making the compound more hydrophilic.

Now a few comments on the previous relationships in tires. It is well known that natural-rubber tires show less abrasion on a wet road than do synthetic-rubber tires, although the abrasion of both is the same on a dry road.

The superior performance of synthetic-rubber tires under wet conditions is explained by the greater attraction for water compared to that of natural-rubber tires, and the consequent stronger interfacial forces, adhesion, and gripping power. On the basis of the concepts stated here, it is now possible to produce natural-rubber compounds which are equally hydrophilic and which have, therefore, the same gripping ability as synthetic rubber.

To get some idea of the effectiveness of the forces which determine the adhesion, it is worthwhile to make a few comments about wetting and wetting power.

THE LAWS OF INTERFACIAL ATTRACTION

The forces which hold together the molecules, the building stones of the substance, completely satisfy each other in the interior, but not at the surface. Consequently all the surface molecules experience an inwardly directed pull. They are subjected to surface tension. A familiar experiment with a soap

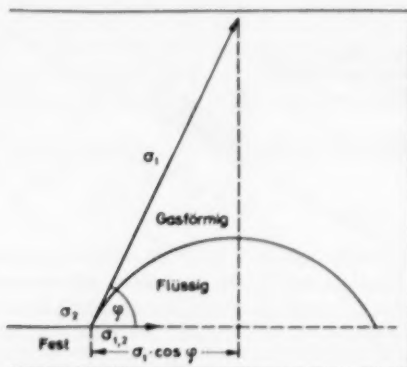


FIG. 2.—Equilibrium of forces for a water droplet on a solid surface. Gasförmig means gaseous phase. Flüssig means liquid phase. Fest means solid phase.

bubble in a rectangular wire frame demonstrates the surface tension, if one side of the rectangle is moveable and if when the rectangle is held in a vertical position the soap film is able to support the little wire rider. If the length of this piece is 1 cm., then the force acting is equal to twice the surface tension in dynes per cm.

Not only liquids, but solids as well, have a surface tension, although it is far greater in solids and not capable of direct measurement, except possibly in very precisely controlled tensile tests under very clean conditions. The forces, for example, which act on water droplets on a rubber underlayer and the nature of this action, are shown by the vector diagram in Figure 2. The tangent to the water droplet and the rubber surface intersect in the boundary angle ϕ . At the rubber surface and parallel to it, there is the surface tension σ_2 (rubber-air) and, in the opposite direction, the interfacial tension $\sigma_{1,2}$ (rubber-water). The difference between the two forces is represented by the projection of the arrow σ_1 , the surface tension (water-air). This projection is the product $\cos \phi \cdot \sigma_1$.

Due to the equilibrium reached by the forces, the contact angle obeys the

following relation, discovered by Young:

$$\sigma_2 - \sigma_{1,2} = \sigma_1 \cos \phi = B$$

where B is the wetting power. To obtain a large wetting force, it is necessary to choose σ_2 as great as possible and $\sigma_{1,2}$ small.

In the case of a solid, σ_2 and $\sigma_{1,2}$ are hard to derive. However, in view of Young's law, the indirect method of testing the wetting tension by measuring σ_1 , the surface tension of water, and the cosine of the contact angle can be used. According to the equation, the wetting force is greater, the smaller the contact angle at constant σ_1 . Accordingly, with water, for example, the maximum wetting force ($\cos \phi = 1$) $B = \sigma_1$ is 73 dynes per cm. at 20° C.

Fortunately water has by nature a high surface tension, and gives, therefore, a very large wetting power when the underlayer (substrate) is completely wetted.

The sole decisive magnitude for the attraction of two media, here rubber and water, is the adhesion, but this depends in a simple way on the wetting force.

The adhesion and also the wetting energy give a measure of the magnitude of the molecular forces which produce the attraction. The adhesion is derived from the considerations involved in the setting up of a boundary surface problem, that is, an interface.

The work of formation of a common boundary surface between two substances is the combination of the work required for the formation of the free surface of the first material, i.e., water, plus the work required to form the free surface of the second substance, rubber, minus the amount of energy A which is liberated by bringing together the two free surfaces. Energy A is liberated because the surface forces now mutually saturate each other, and the stored surface energy released appears as A . This is expressed formally as:

$$\sigma_{1,2} = \sigma_1 + \sigma_2 - A$$

or the value sought:

$$A = \sigma_1 + \sigma_2 - \sigma_{1,2}$$

that is, the adhesion is equal to the sum of the surface tensions minus the interfacial tension.

From $\sigma_2 - \sigma_{1,2} = B$ follows:

$$A = B + \sigma_1. \quad \text{Adhesion} = \text{wetting force} + \sigma_1.$$

Hence, in a system with the same liquid, having surface tension σ_1 , the adhesion is directly proportional to the wetting force.

But what happens when wetting agents are added to the water? The surface tension of the water then decreases, the wetting relationships (contact angle ϕ) not only do not become less favorable, but, on the contrary, actually improve. Based on the relations:

$$A = B + \sigma_1 = \sigma_1 (1 + \cos \phi)$$

in this case the adhesion A becomes smaller. In spite of complete wetting, both the adhesion and the wetting force are only equal to the decreased surface tension, for example, of a soap solution.

The change of the sliding angle measured with the inclined plane confirms the decrease of adhesion and, therefore, of the coefficient of friction. Further,

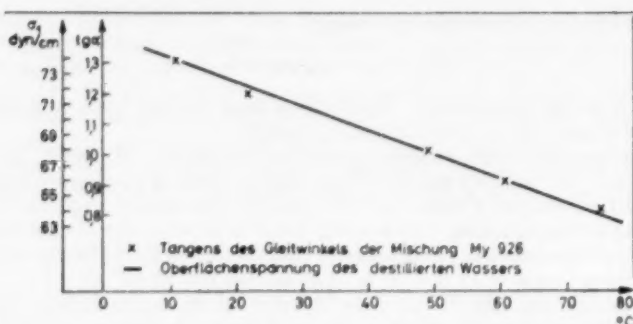


FIG. 3.—Relation between the coefficient of friction $\tan \alpha$ and surface tension of distilled water as a function of temperature. X Tangent of slide angle of compound My 926. — Surface tension of distilled water.

the experiment with a soap solution shows that it is necessary to distinguish between wettability and wetting force.

SIGNIFICANCE OF THE WETTING FORCES FOR RUBBER-WATER AND WATER-ROAD

To obtain the highest possible coefficient of friction between rubber and water in practice, where the liquid, i.e., water, has a given fixed surface tension, the emphasis should be put on a large σ_2 value, the surface tension of the rubber. Increasing σ_2 gives, with constant σ_1 , a diminishing contact angle ϕ , and, hence, a greater wetting force $\sigma_1 \cos \phi = B$, while at the same time $\sigma_{1,2}$, the interfacial tension, decreases. According to this view, the wetting force and the resulting adhesion depend in great measure on the composition of the rubber compound.

The fact that materials that bloom out decrease the friction coefficients is simply explained by the lowering of the surface tension of the rubber. The rubber is in fact, no longer the true surface, because a bloomed surface with a new lower surface tension is formed.

The effect of wetting on the chemical surface condition is an extraordinarily

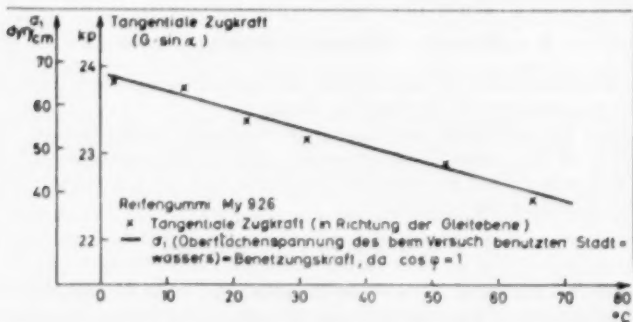


FIG. 4.—Dependence of the coefficient of friction on surface tension of the liquid. Right-hand ordinate Tangential tractive force ($G \cdot \sin \alpha$). Compound My 926. X Tangential tractive force (in direction of the inclined plane). — σ_1 (surface tension of the tap water used) = wetting force, since $\cos \phi = 1$.

sensitive one, and, with the aid of the wetting of the rubber with water, predictions can be made about the coefficients of friction to be expected on the basis of the wetting phenomena. For example, suppose one were to test the surface with a fountain pen containing a definite volume of water, and to measure the length of the line until the water is used up. Types that are wettable permit drawing continuous lines.

If we compare the surface tension of water with the coefficient of friction of a readily wettable rubber with increasing temperature, we find, as shown in Figure 3, complete agreement in the course of the two values. There is the same agreement in the trend of the two values in the case of water having a lowered surface tension.

The wetting force, that is, $B = \sigma_1$ (complete wetting) can again be brought into direct relation to the friction value, in accordance with Figure 4. The tangential tension ($G \cdot \sin \alpha$) chosen as ordinate is equal to the friction according

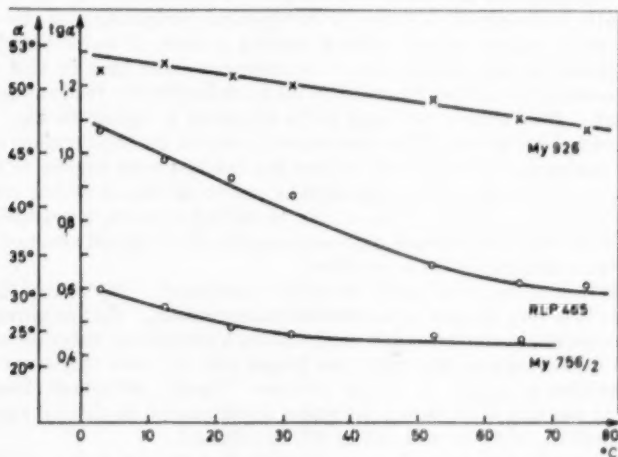


Fig. 5.—Dependence of the coefficient of friction on the rubber compound.

to Figure 1, but in the opposite direction. Comparison of the two ordinates with their scales gives the decrease of friction per unit decrease of surface tension.

In compounds containing substances that tend to bloom, the behavior (see Figure 5) shows complete agreement between surface tension and coefficient of friction in a more pronounced drop at the lower initial part and a subsequent flattening out. This is explained by solution of the bloomed film on the rubber in the hot water, or by the reabsorption of the bloomed substance by the rubber at the higher temperature.

As is well known, conditions of driving are especially dangerous when it is just starting to rain. The interfacial conditions can provide the explanation for this, for comparative tests always show very poor initial wetting of a dry rubber sample. This condition disappears at different rates with different rubber compounds. The air adsorbed on the surface lowers the wetting power with respect to water. This air is thus responsible for greater skidding danger.

HYDROPHILIC RUBBER COMPOUNDS AND HYDROPHILIC ROAD SURFACES

What has been said so far about the system: solid-liquid-air (tire-water), is also valid for the system: road surface-water, and, consequently, for the system: road-water-rubber, as well. In general, the clean surface, i.e., the true surface of the solid body, should possess a high surface tension and, hence, a high wetting force, so that a tire developed to resist slipping on a solid underlayer must show good gripping ability.

In view of the above considerations, a skidproof road would be characterized by strong attraction to rubber by way of water, in that it possesses great wetting power by water, due to its surface material construction, as a result of which oily residues and other hydrophobic contamination are displaced automatically by the water itself, i.e., by rain, without the use of expensive cleaning agents.

Experiments show that on a road surface contaminated with oil or one that is inherently hydrophobic because of its chemical composition, water droplets are very easily moved about without leaving a trace of water behind. The wetting power is very slight, and it is understandable that in this case the holding tendency to rubber via water in the boundary layer: road surface-water, is deficient. Here even a tire built to be skidproof is certain to slip.

The road chemist can aid by the correct choice of the road surface material, in a way analogous to the activity of the tire chemist with respect to the tires.

The above ideas should be applicable as well to all uses of rubber where friction, or conversely, sliding, plays a role (a sliding support, windshield wiper, etc.). These boundary surface physical considerations should also not be overlooked where slipping on ice is involved.

In this connection, blue basalt should be mentioned. Because of its surface properties, it is very dangerous to modern transportation. Its fine pored surface makes it capable, in the dry state, of absorbing hydrophobic substances. Once these are in the surface, the rain is no longer able to clean this stone surface, and it remains a danger to motor vehicles. Easily performed, inexpensive methods of cleaning such stones are under development, so that an appreciable improvement in safety from skidding will be attained.

Unfortunately it is true of every material that its own true surface in the presence of air is only short-lived, and, in just the same way, cleaned blue basalt stones for the most part, depending on how heavy the traffic is, do not long retain their clean surface unless the cleaned stone is kept constantly wet. The burning off of the stones, which has been tried so far leads, on repeated treatments, to destruction of the stone surface or of the stones themselves.

The effectiveness of a distinguishable degree of wetting power is documented also on such blue basalt stones in the following experiment.

A stone taken from a road surface with poor wetting power gave, in the laboratory, a sliding angle of 32°. A much smoother surface cut from the same stone, gave, with good wetting and the same rubber, the angle 49°. Blue basalt is thus inherently a nonskid road material, but for it to remain equally good in the long run, the surface pores must be plugged with hydrophilic material, or else regular periodic cleanings must be carried out.

One obtains the best idea of the importance of the wetting power for the skid resistance of tires when one realizes that, in spite of all improvements in compound formulation and in tread pattern, the gripping tendency on wet blue basalt roads still leaves something to be desired.

In order to obtain good gripping power, it is, therefore, necessary to strive for the greatest possible adhesion, i.e., wetting power for road surfaces as well as for tires. To this end one should:

1. Avoid as far as possible measures which make the rubber or the road surfaces water repellant and if these are necessary for other reasons, at least to apply them with caution;

2. Adopt measures aimed at making the road and rubber surfaces definitely hydrophilic.

We have today the means of producing tires of either natural rubber or synthetic rubber which possess good wetting power. The gripping power of these tires has been found to be excellent, both in tests on the road and on the test stand.

STUDIES ON ABRASION AND WEAR OF RUBBER. I. THE CHEMISTRY OF CARBON BLACK AND ITS EFFECT ON ABRASION AS DETERMINED BY THE NATIONAL BUREAU OF STANDARDS METHOD *

V. A. GARTEN, K. EPPINGER, AND D. E. WEISS

DIVISION OF INDUSTRIAL CHEMISTRY, COMMONWEALTH SCIENTIFIC AND
INDUSTRIAL RESEARCH ORGANIZATION, MELBOURNE, AUSTRALIA

INTRODUCTION

In earlier work on the nature of chemisorptive mechanisms in rubber reinforcement, Garten and Sutherland¹ found that carbon blacks react to different extents with free radicals, and the number of active sites per unit area for the various carbons was derived from the experiments. It was suggested that the free radicals, produced from the breakdown of rubber during mastication, could form chemical bonds with the filler particles and thus produce a rubber-filler network. Since the majority of the mechanical properties of filled rubbers, for example, modulus, hardness, and resilience, are controlled by the total number of chemical bonds connecting polymer chains, an analysis of a network which includes filler-rubber bonds predicted a linear relation between the modulus of a reinforced rubber and the quantity σ/r , where σ is the number of active sites/unit area of the filler and r is the radius of the filler particle. The relation was confirmed by experiment. There was, however, little indication of any simple relationship between the abrasion resistance of a reinforced rubber and the mechanical properties of its network, when determined by the degree of cross-linking. It was suggested that the abrasion resistance of a rubber compound was controlled by its chemical stability, particularly towards oxidation, and the possible catalytic effects of various fillers on such chemical changes.

For a tire of natural rubber reinforced with carbon black, there is an abrasion loss of at least 60 g./1000 miles of road service. Without reinforcing, the loss is 30-40 times as high. Despite other disadvantages, rubber containing no unsaturated groups, for example, the isocyanate type, is known to have at least twice the life of reinforced natural rubber tires. This type of rubber does not require filler reinforcement. The extraordinary differences in the lifetimes, which are in the proportions of 1:35:70, of a pure-gum vulcanizate, a reinforced natural rubber, and an unreinforced isocyanate rubber with approximately the same mechanical properties indicate that the resistance cannot be described by these properties as measured for the original rubber, although the final shearing off of particles from the surface will be determined by some mechanical property or properties of the chemically changed rubber. With natural rubber or any unsaturated synthetic rubber, an antioxidant is essential for long service life, whereas saturated rubber needs no protection.

The study of the mechanism of abrasion as it affects the service life of tires is difficult because no reliable laboratory method exists for the assessment of

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service life. On the other hand, no better test can be designed as long as the mechanisms of abrasion and the action of fillers are not understood. We have investigated the fundamental chemical properties of carbon blacks, their catalytic properties, and their effect on abrasion as determined by the National Bureau of Standards (N.B.S.) technique. This choice of method was made because of its ready availability in the laboratory of Dunlop Rubber Australia Ltd., where abrasion tests were being regularly performed. Since we believe that abrasion is concerned with the oxidation of rubber, attention was paid to the behavior of carbon blacks in oxidation reactions and to the chemical character of the black.

Both activation and inhibition of the oxidation of rubber by carbon black have been reported. Winn, Shelton, and Turnbull² described increased rates of oxygen absorption with increase in surface area of the carbon. They attributed the correspondingly great deterioration of physical properties of GR-S vulcanizates as the result of the greater oxygen uptake. Kuzminskii, and coworkers³, working with unvulcanized, unstabilized butadiene-sodium polymers, showed that increased amounts of channel black reduced the rate and amount of oxygen uptake. They deduced from these results that the action of carbon black was to inhibit the normal chain reaction induced by rubber-peroxyg. Increased rate of oxygen uptake observed by Winn, Shelton, and Turnbull² can be explained by the adsorption of added antioxidant on the carbon black surface.

Sweitzer⁴ and Sweitzer and Lyon⁵ were able to provide convincing evidence that carbon black inhibits chain scission during mastication in a Banbury mixer, and they suggest that this may result from the interaction of free radicals with the carbon surface. The possible effect on abrasion of a similar action of carbon black in vulcanized rubbers was not considered. Van Amerongen⁶ studied the effect of carbon blacks on oxidation, hysteresis, and wear of natural rubber. The rate of oxidation and the solubility of oxygen increased with surface area of the black, as did hysteresis losses and heat build-up, resulting in loss of tensile strength and elongation. The author referred to the common concept that smaller particles give higher reinforcement, although with some channel blacks with surface areas higher than most furnace blacks lower wear resistance is obtained. It is stated that, with carbon blacks showing higher hysteresis loss or heat build-up, a higher wear resistance is obtained "apparently because the weakening effect of higher temperature resulting from higher hysteresis losses is only of secondary importance compared with the more direct effect of blacks of smaller particle size on those mechanical properties of rubber which are important for wear resistance". It is somewhat difficult to see what "mechanical properties" are important, since no relation is known to exist between abrasion resistance and any other physical property of a reinforced rubber compound. ¶

The following experiments were designed to test our theory of oxidative breakdown as the major cause of rubber abrasion. The systematic results on the chemical structure and catalytic properties of a series of carbon blacks of approximately constant surface area strongly suggest that the inhibition of peroxidation of a rubber compound by an active filler is to be regarded as an essential feature of "reinforcement".

MATERIALS AND METHODS

Batches (200 g.) of an ink black of relatively high surface area (675 m.²/g.) and of low suspension pH (3.9) were heated for 2 hours in pure nitrogen in the

temperature range from 200–1000° C and allowed to cool without the admission of air.

Surface areas were determined by the B.E.T. method, using nitrogen as the adsorbate. Ultimate analyses were performed by the usual microanalytical procedures and the oxygen assay was done by a direct method. Total iron was determined colorimetrically with 5-sulfosalicylic acid, after destructive oxidation of the carbon matrix with $\text{H}_2\text{SO}_4\text{-HNO}_3$. The amount of iron that could be extracted with sulfuric acid was measured by the same method after shaking 5.000 g. carbon with 50 ml. 2N H_2SO_4 at room temperature for 1 hour and centrifuging. The adsorption of acid and of alkali on the heat-treated black was determined in the manner previously described⁷. Adsorptions were also determined after treatment of the carbon blacks with an excess of neutral doubly-distilled hydrogen peroxide and subsequent washing by decantation (1.00 g. carbon suspended in 5 ml. neutralized H_2O_2 , 50 vol. for 24 hours).

The catalytic ability of a carbon black to decompose hydrogen peroxide is determined by the oxidation state of the surface of a black, so it seemed desirable to investigate the change in the carbon surface after reaction with hydroxyl-free radicals produced from hydrogen peroxide. The decomposition of hydrogen peroxide was tested in a Warburg apparatus at 25° C. Black (0.050 g.) was moistened with 2 ml. of 0.001 N K_2SO_4 and left standing overnight to expel gases adsorbed on the carbon surface. An absorbent for carbon dioxide was placed in the center compartment and the side-arm charged with 0.4 ml. of a 0.1 per cent H_2O_2 solution. To differentiate between the catalytic activity of the carbon and any effect of an iron impurity, the experiments were repeated after treatment with cyanide (the carbons were wetted with 1 ml. of 0.001 N KCN + 1 ml. 0.001 N H_2SO_4).

Further information on the nature of the surface could be deduced from measurements of the magnetic susceptibility. A Gouy balance of maximum field strength of 10 kg. was used at room temperature and the results were extrapolated to infinite field strength. The densities of samples were determined by the flotation method, using mixtures of bromoform and benzene.

For the abrasion tests, the various carbon blacks were milled into rubber to produce a test mixture of the following composition: Rubber (No. 2 smoked sheet), 100; stearic acid, 2; pine tar, 3; carbon black, 50; zinc oxide, 5; sulfur, 3; mercaptobenzothiazole, 0.8. No antioxidant was added, to preserve antioxidation effects caused by the carbon itself. All samples were 0.5 inch thick and were cured for 60 minutes at 142° C, after which time they had approximately the same Shore hardness of 75–77. All samples were given 50 revolutions on the N.B.S. abrasion machine.

The essential features of the machine are as follows: Garnet paper No. 2½ is held by rubber bands on a rubber-coated metal drum 6 inches in diameter, which is rotated at 40 r.p.m., the revolution of the drum being indicated by a counter. Three test-specimens, 1 inch square and approximately 0.25 inch thick, are cemented to small fiber disks, which in turn are fastened to weighed arms (downward force of 5 lb.). Dial gauges, graduated in thousandths of an inch, are used to indicate reduction in the thickness of the specimens. Compressed air is used to keep the abrasive surface clean. Before making a test run, the specimens are allowed to wear until the surface conforms to the shape of the drum.

Particular attention was paid to the oxygen content during compounding and vulcanization, as well as in the process of abrasion.

TABLE I

Ink black heated for 2 hours in pure N ₂ at °C	C (%)	H (%)	O (%)	N (%)	Ash (%)	Total iron (% × 100) (% × 100)	Iron extracted with 2N H ₂ SO ₄ (% × 100)	Surface area (B.E.T.) (m. ² /g.)	μ-Equiv./g.		μ-Equiv./100 m. ²	
									NaOH	HCl	NaOH	HCl
—	80.12	1.81	15.5	<1	0.04	3.8	0.4	675	1167	24	172.9	3.56
200	82.43	1.71	13.5	<1	0.03	4.0	0.4	645	1167	43	180.9	6.07
300	82.22	1.64	13.4	<1	0.02	3.6	0.4	670	1113	64	166.1	9.55
400	83.16	1.65	12.9	<1	0.08	2.8	0.4	665	1033	82	164.4	12.3
500	85.92	1.91	13.0	<1	0.06	2.8	0.6	695	857	109	123.3	15.7
600	88.70	2.35	9.3	<1	0.06	2.8	2.2	715	485	165	67.8	23.1
700	93.79	1.46	4.17	<1	0.06	4.4	2.2	730	238	243	32.6	33.3
800	95.0	1.71	3.05	<1	0.06	4.0	4.0	710	166	309	23.4	43.5
900	98.0	0.60	2.40	<1	0.09	4.0	3.7	670	130	309	19.4	46.1
1000	98.9	0.60	1.29	<1	0.02	4.0	4.0	615	121	291	19.7	47.3

RESULTS AND DISCUSSION

Garten and Weiss⁷ have shown that sugar char has a hydroquinone character when prepared at 400° C, but develops a quinonoid structure at 800° C. They also showed that carbon blacks are chemically similar to sugar chars. Channel and ink blacks were shown to contain hydroquinone groups, whereas furnace blacks were quinonoid. On heating the carbon from 400 to 800° C, some quinone groups may be created by dehydrogenation. It was suggested, that carbons intermediate between the two extremes should contain a maximum amount of semiquinone-type oxygen, possibly in resonance with C sites. It was also suggested that resonance might reasonably be expected to extend over the whole conducting structure of the carbon. The detailed mechanism of this

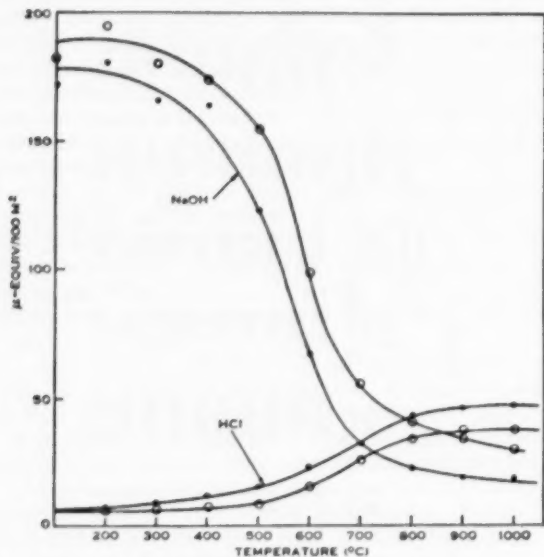


FIG. 1.—Effect of heat treatment of carbon black on acid- and alkali-adsorption. ● Original; ○ After contact with hydrogen peroxide.

conductivity is obscure. Winslow, Baker, and Yager⁸ have proposed, from paramagnetic resonance studies, that the conductivity arises from the drifting of radical sites, as in certain types of semiconductors. The present work suggests that both semiquinone groups and C radicals might be involved in this mechanism, and that, furthermore, contamination by transition metals, particularly iron, may play an important part.

In the region of 500–800° C there is also a characteristic small change of surface area as observed by Boyer and Foucault⁹ and confirmed in the present series of experiments (see Table I).

Figure 1, showing the adsorption of acid and alkali/100 m.² of carbon surface, indicates that equal adsorption of acid and alkali occurs in the region of 700° C, which, from previous considerations, could be identified with a semiquinone configuration. Figure 1 also shows that treatment of the various blacks with hydrogen peroxide resulted in a shift of the maximum semiquinone con-

centration (with its equal adsorption of acid and alkali) from the 700° C-black to that activated at 850° C.

The observed changes in magnetic susceptibility with the temperature of activation are shown in Figure 2. The results were extrapolated to infinite field strength, which eliminates the effect of ferromagnetic impurities¹⁰, so that the

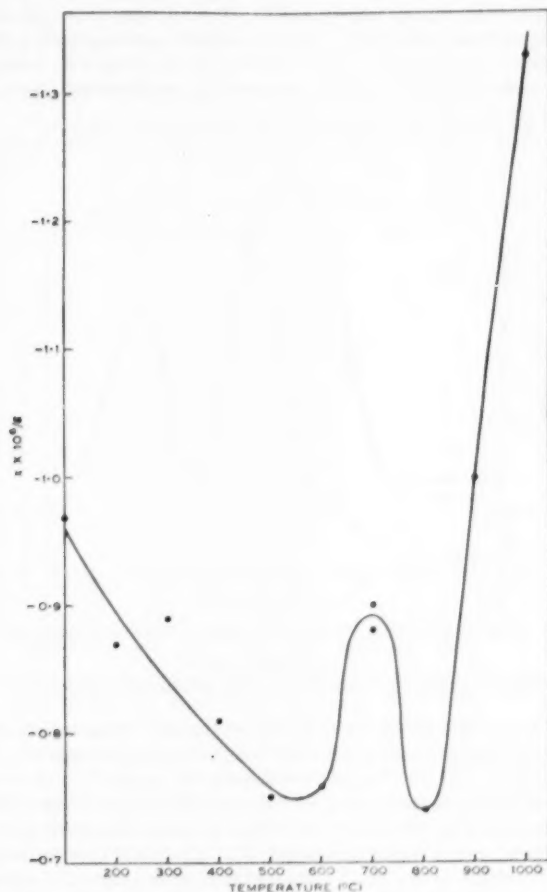


FIG. 2.—Effect of heat treatment of carbon black on magnetic susceptibility.

figures represent the susceptibilities inherent in the structure of the carbon. The hump observed at 700° C most likely reflects the weakening of the paramagnetic contribution of the single electron groups through spin-interaction with the ferromagnetic impurities. This is supported by the Figure 3, which shows a distinct minimum of the effect of ferromagnetic impurities at 700° C. Extraction with 2N H_2SO_4 yielded 50 per cent of the total iron present in the carbon that had been prepared at 700° C, whereas 80 and 100 per cent could be

extracted from the carbons heated to 600 and 800° C, respectively (Table I). At this juncture it would be mere speculation to suggest any particular explanation for the effect of the iron on the carbon. There is the distinct possibility of Fe—C bonds, as in carbides. Since the absolute absence of nitrogen has not been proved, there is also the likelihood of Fe—N bond formation, as shown by Rideal and Wright¹¹. Iron could also exert its effect via the C—O bonds in the manner proposed by Long and Sykes¹². It may also be recalled⁷ that with paramagnetic carbons a minimum in paramagnetic susceptibility was found in the same temperature region. The relation of the magnetic susceptibility to the catalytic activity of the various carbons will be discussed presently.

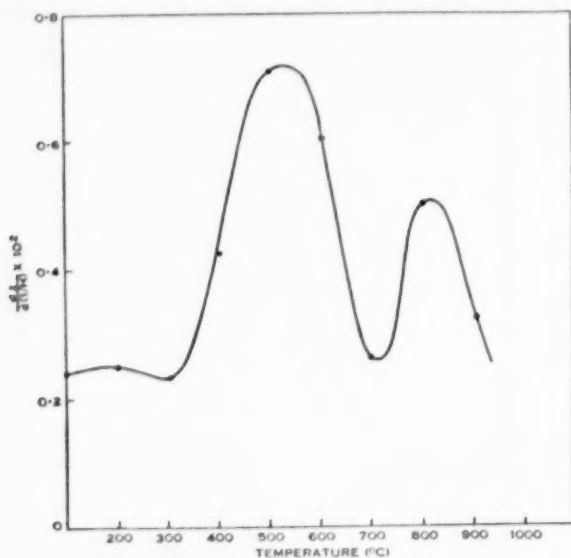


FIG. 3.—Effect of ferromagnetic impurities on magnetic susceptibility.

In recent years, the significance of the electronic characteristics of solids in relation to their catalytic activities has been particularly stressed by Rienaecker and Bade¹³, Couper and Eley¹⁴, and Dowden and Reynolds¹⁵. More specifically, the presence of electrons with unpaired spin should become apparent in reactions which are controlled by the rate of transfer of single electrons between a solid catalyst (carbon) and a liquid substrate, e.g., hydroxyl free radicals produced by the decomposition of H_2O_2 . It is generally agreed that the increase of rate of decomposition of H_2O_2 by transition metal ions¹⁶, or metallic alloy catalysts¹⁶, and also the decomposition of organic peroxides in the so-called redox-activation¹⁷ in the presence of traces of heavy metals is due to the initiation by the reaction:



This requires that the rate of decomposition in the presence of carbon black catalysts should increase with the number of unpaired electrons. Experimental results obtained with carbon black heated at different temperatures in nitrogen are shown in Figure 4. The rate of decomposition of H_2O_2 is a maxi-

mum with the carbon black activated at 900° C. This might arise from the introduction of further hydroxyl groups to the surface from the decomposing hydrogen peroxide with the semiquinone equilibrium shifting to the higher temperature region. The manometer readings given are those obtained after 230 minutes, since with longer periods the gas pressure began to decrease, owing to slow oxidation of the carbon black to CO_2 . Thus a sample of carbon black, outgassed in high vacuum for several hours and treated with H_2O_2 , evolved gas containing 0.74 per cent CO_2 . Adding cyanide had a negligible effect on this catalysis.

A process similar to that given in Equation (1) for the decomposition of hydrogen peroxide may thus arise from the irreversible combination of one $\cdot\text{OH}$ radical with the carbon surface, leading the second $\cdot\text{OH}$ radical to initiate a chain reaction.

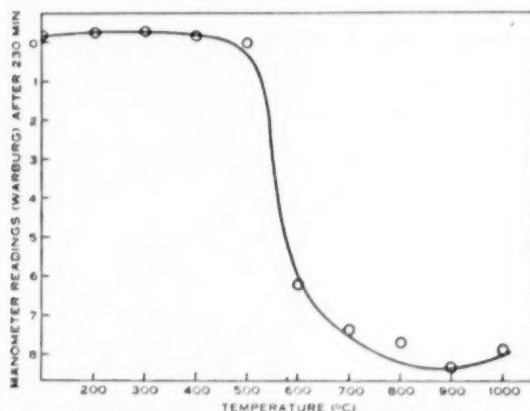


Fig. 4.—Rates of hydrogen peroxide decomposition by heat-treated carbon black.

It is generally agreed that laboratory abrasion machines operate under unduly severe conditions, and that sticky surfaces often arise on the test-piece, leading to fictitiously low figures from clogging of the abrasive. Even when no smearing can be detected, the abraded rubber surface presents a peculiar array of parallel ridges proceeding perpendicular to the direction of abrasion, which Schallamach¹⁸ called the "abrasion pattern" and which he related to the normal load and the mean radius of curvature of the abrasive particles.

If the plasticized rubber surface, consisting of broken chains, is given a chance to recover, it will do so to a marked degree even in the presence of air. Plate 1, depicting two abrasion test samples after an abrasion test, shows that with intermittent abrasion in the absence of a stream of air some of the abraded chips reweld and thus produce the characteristic formation at the far end of the abraded surface. This phenomenon appears similar to that described by Outwater and Shaw¹⁹ when grinding steel in an inert atmosphere. Those authors showed that the grinding forces required were unusually high, sometimes 25 times as high as the corresponding values in air. In the absence of oxygen, the steel chip rewelds to the finished surface as it curls back on the work, and because of this the same metal may have to be sheared several times before it finally leaves the system as a free chip. This phenomenon plausibly

explains why the energy required to abrade rubber is so much higher than the theoretical maximum energy required to break chemical bonds and by tearing out particles from the rubber to create new surface²⁰.

There seems to be little doubt that both smearing and the development of abrasion patterns are caused by plastic flow similar to that observed during mastication in a mill. If abrasion breaks the chains of the rubber, then the

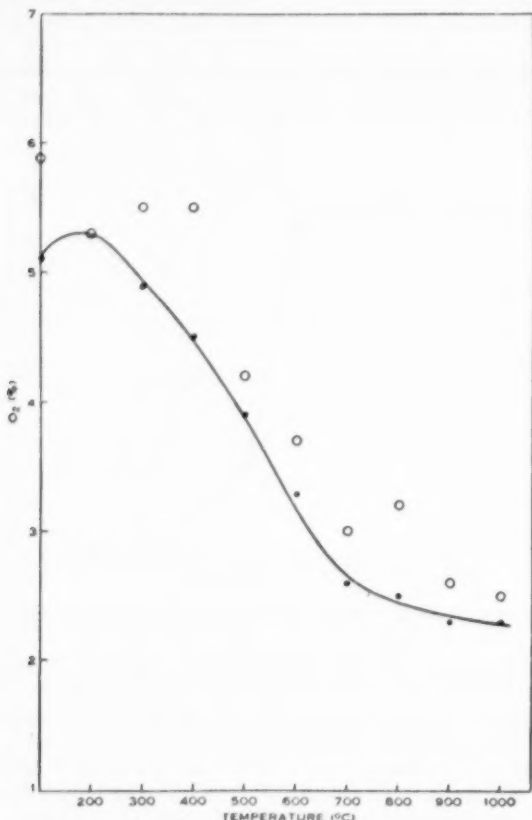


FIG. 5.—Oxygen contents of rubber compounds, prepared with heat-treated carbon blacks, before and after abrasion. ● Parent rubber; ○ Abraded chips.

free radicals produced recombine rapidly, but a relatively small number react with the oxygen of the air to produce plastic material which will be rubbed off.

The oxygen content of the abraded flakes or chips is always higher than that of the parent rubber samples (Figure 5). The somewhat erratic results might be due to contamination of the microsamples by grit particles of the abrasive. It is obvious, however, that during abrasion the rubber picks up oxygen at an extraordinary rate.

Results of a limited number of abrasion tests (three runs each) are given in Figure 6, which also indicates the fluctuation of tests. Within the limits of

variation there are two distinct minima in abrasion loss: that with the virgin material and that with the black obtained after heating to 700° C in nitrogen. It is possible that the protection provided by the strongly acidic untreated carbon black is due partly to its polyphenolic character which enables it to act as an antioxidant in a fashion similar to that suggested by Bolland and Ten Have²¹, the essential requirement being the conversion of an active chain carrier to a stable product, which may or may not have a free radical character.

The pronounced effect of the 700° C-carbon (see Figure 6) cannot be described in the conventional terms of antioxidant activity, for example, by destroying active hydroperoxide free radicals, as no known antioxidant can satisfactorily replace the carbon black. It is assumed that the increase of abrasion resistance is due to recombination of the products of chain scission, it would be logical to assign the action of the higher temperature carbons to their reaction with the depolymerization products. With rubberlike materials, peroxidation has been shown to be the prerequisite of molecular breakdown responsible for an amazing fall in the molecular weight²². Although the scission

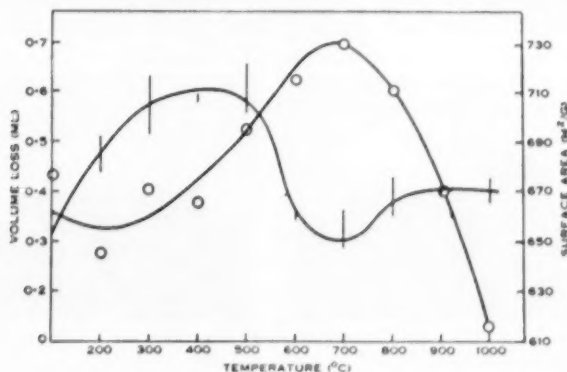


FIG. 6.—Surface areas of heat-treated carbon blacks and abrasion resistance of rubber compounds, prepared with them (volume loss in ml. after 50 revolutions on N.B.S. abrasion machine).

sets in unpreventably during the adsorption of oxygen, even at room temperature, a reasonable rate of reaction usually requires thermal promotion. The immediate products of peroxide decomposition are invariably active free radicals, some of which may not react readily with oxygen but rather combine with a carbon surface. It is also conceivable that such primarily formed bonds between carbon and rubber may eventually in the course of further shearing action break up again and allow some of the original chain fragments to recombine. It would be in this indirect, catalytic fashion, that the polymer is protected against the attack of oxygen and thus prevented to a marked degree from depolymerization, with formation of viscous and tacky breakdown products.

The question as to how to improve abrasion resistance can thus be reduced to the more precise one as to how to protect an unsaturated rubber compound against depolymerization. The problem, reformulated in this manner is, of course, closely related to the one concerned with aging and the general study of the action of antioxidants, where particular attention will have to be paid to antioxidants of the oxidation-reduction type.

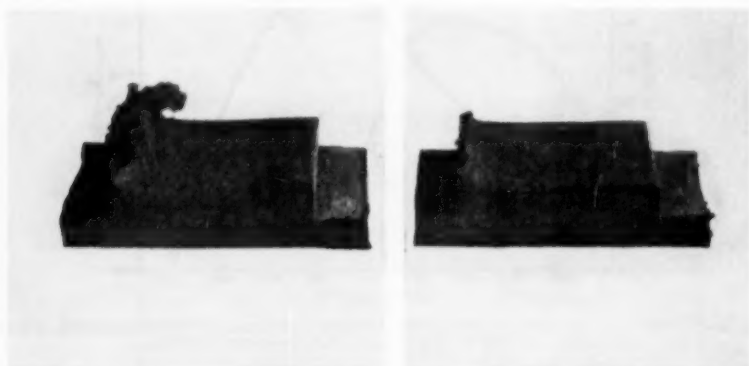
SUMMARY

A series of carbon blacks of approximately constant surface area were prepared by heating a strongly acidic carbon black in N_2 in the range of 200–1000° C. Their adsorption capacity for alkali and acid, catalytic behavior in H_2O_2 decomposition, and magnetic susceptibility have been studied and related to their effect on abrasion resistance when incorporated into a standard tire tread stock in the absence of antioxidants.

It is suggested that there are, at least, two distinct chemical mechanisms by which carbon blacks can produce reinforcement, that is, by their (irreversible) action as polyphenol type antioxidants (acidic = low-temperature blacks), or in a catalytic (reversible) fashion through temporary stabilization of broken rubber chains on their surface (neutral = medium-temperature blacks).

ACKNOWLEDGMENTS

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Effect of abrasion conditions on surface structure of slightly undercured rubber. Left: Intermittent abrasion (10 min.) without stream of air. Right: Continuous abrasion (10 min.) in stream of air.

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TIRE WEAR AND FUEL CONSUMPTION *

H. C. J. DE DECKER, G. J. VAN AMERONGEN,
AND J. F. BENDERS

RUBBER-STICHTING, DELFT, NETHERLANDS

WEAR

WEAR AND ITS PRACTICAL SIGNIFICANCE

Wear of a tire tread is the loss of material from its surface as a result of movement on the road. It is not possible to reduce the wear of a tread by using lubricants because the tread must satisfy a number of different and conflicting requirements at the same time. The tread must, on the one hand, guarantee nonskid contact with the road, yet on the other hand it must absorb elastically all the irregularities of the road. Finally there is another requirement, namely, that the tread show minimum wear. Except for vulcanized rubber containing certain active fillers, there are no other materials which satisfy these contradictory requirements.

MEASUREMENT OF WEAR

It has been attempted many times to measure the wear of a tread surface with a laboratory apparatus. The investigations have, however, not made it possible to predict the behavior of a tire in service. As a result, attempts have been made for a long time to determine wear in actual service. Here two difficulties arise. The first is that one must have available a quantitative measure of wear. This difficulty can be overcome by weighing the tire or by measuring the depth of the profile grooves. The determination of the weight is much more exact than that of the average depths of the grooves, so that by the weighing method it is possible to carry out experiments with fewer kilometers of travel. The second difficulty is the fact that service conditions have such a pronounced influence on wear that, with different conditions, the kilometer values obtained can show great discrepancies, even for the same tires. There are two methods of avoiding the latter difficulties. The conditions can be kept as constant as possible during the experimental run, for example, by determining the total kilometers on a definite test route, with the same driver throughout and under the same weather conditions. Furthermore one can disregard all the conditions of service and seek to exclude their influence by obtaining a mean value from a very large number of measurements.

The second method is not considered because such a mean value is not reliable and the method is very expensive.

The basic principle in wear measurements is the comparative measurement of different tires, which are mounted on a single vehicle, and which are interchanged after a certain number of kilometers. The great influence of wheel position on the vehicle on wear, by which differences up to 80 per cent in results may appear, is thus excluded. If the maximum yield of the measurements is to

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be secured it is necessary to keep the conditions of travel after each tire change as near alike as possible.

There is also another method that can be used to compare two treads of different compositions. It is to make up the tread surface in several sections of different tread compounds. In practice, several difficulties arise in these methods, although they can give exact results. In this sort of measurement, the wear can be determined only by the depth of the profile grooves.

Table I gives an example of a complete experiment which we designate as a "standard wear test". The total travel was about 2000 km. (500 km. per period). We can conclude that there are suitable methods of measuring wear. However, it must not be expected that there is any way by which the absolute service life or the absolute wear resistance can be determined with satisfactory

TABLE I
EXAMPLE FOR A COMPLETE WEAR TEST (F 30)

Wear measurement	Treads			
	V	A	B	C
Periods $\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \\ 4 \end{array} \right.$	47.8	44.4	46.7	43.3
	54.4	37.8	34.4	32.2
	55.4	57.6	32.2	29.9
	42.1	42.1	23.3	44.3
Wear (geometric mean)	49.6	44.9	33.2	36.8
	$\left(\frac{49.6}{44.9} \times 100 = 110 \right)$			
Relative wear resistance	100	110	149	135
Reliability factor (from 16 measurements) $p = 0.91$	$(0.91 \times 110 = 100; 1/0.91 \times 110 = 122)$			
Reliability range (90% statistical certainty) $\left\{ \begin{array}{l} \text{from} \\ \text{to} \end{array} \right.$		100 121	136 163	123 148

accuracy. The only property that can be determined with even fairly satisfactory exactness is the relative wear resistance under chosen conditions. This is represented by the following relation:

$$R = \frac{\text{Wear of the comparison tire}}{\text{Wear of the test tire}} \times 100$$

NATURE, ACCURACY, AND SIGNIFICANCE OF THE WEAR TEST

Wear measurements should lead to results which bear some practical relation to the normal use of the tire. The normal use of a tire is naturally a rather undefinable concept. However, if one compares the average wear in normal use with that under special conditions, one obtains at least a starting point for the determination of normal use.

When one defines the intensity of the wear experiment as the average absolute amount of wear of the standard tire to be tested, then this degree of severity should correspond as closely as possible to the average amount of wear of similar tires in regular service. Of course then the severity of the test cannot be the same in different countries and at different seasons of the year. The severity will depend on the following conditions:

- (1) Chance variations, defects in manufacture of the tire, unbalanced mounting and spring arrangement, non-uniform braking, etc.
- (2) Type of driving (manner of accelerating and braking, speed).
- (3) External circumstances (road surface, curves, steepness of grades, temperature, moisture).

It has turned out that in a standardized wear experiment the variations mentioned in (1) can be largely eliminated, and that with exact instructions to the test driver and by control with a tachograph, the conditions of (2) above can be held fairly uniform. Further it has also proved possible, by choice of a typical stretch of road together with the above standardization, to obtain a fairly good uniformity of conditions by which a degree of severity of the experiment is made possible which simulates sufficiently well the practical conditions prevailing in the respective countries.

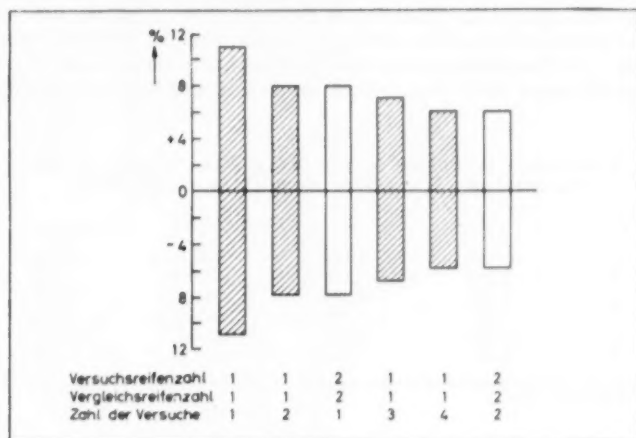


FIG. 1.—Reliability (90% statistical certainty) in percentage of the average wear resistance in the standardized road test.

Number of test tires	1	1	2	1	1	2
Number of comparison tires	1	1	2	1	1	2
Number of experiments	1	2	1	3	4	2

Since normal use defined in this way is only an average value, and certainly extreme values on both sides as well can occur in actual service in every country, wear measurements should be extended to cover much more severe as well as considerably less severe tests. In this connection a very great enhancement of the intensity can be effected, and, moreover, with the same means, by carrying out the test on a racing route, Monthéry, Zandvoord). The severity can be increased fiftyfold, for example. On the other hand, the intensity can be varied by the choice of the motor vehicle and the speed. In normal use the wear is five to ten times less with a little car like the Renault IV than with an American car of average size, e.g., the Ford Mainline.

What value can be placed, now, on the results of the standardized wear experiment? Not only should the variability in the relative wear resistance in the case of repeated tests with the same set of tires under the same conditions be recognized (repeatability), but also the variability of the wear resistance when this is determined with different sets of tires of the same composition

(reproducibility). Furthermore a measure of the reliability of the ratio of length of life for two tires should be found when this ratio is derived from the relative wear resistance obtained in short experiments (extrapolability).

In every standard test each tire is weighed or measured four times. From these sixteen measured values the coefficient of variance of the wear per 1000 km. is calculated. In our measurements this coefficient of variance is about 10 per cent, and is the basis for the calculation of the repeatability of the test. For this the width of the reliability curve serves as a measure. This width depends, not only on the coefficient of variance of wear per 1000 km., but also on the nature of the experiment, in the first place on the number of test tires of one type and the number of comparison tires of one sort per experiment, and in the second place on the number of repetitions of the test with the same tires.

Figure 1 gives a picture of the breadth of the reliability curve with different numbers of tires and repetitions. Having learned from this the importance of repetitions of a test in the reduction of the reliability range, we now turn our attention to the question of the value of repeating the test with new tires of the same type. In this connection we should realize at the outset that all tires of a given type will show deviations in their properties, and therefore in their wear

TABLE 2
VARIATION COEFFICIENT OF THE MEAN WEAR VALUES IN THE
STANDARDIZED WEAR TEST WITH TIRES ON THE ROAD

$k \backslash n$	1	2	3	very large
1	0.142 0.224	0.122 0.212	0.114 0.208	0.100 0.200
2	0.100 0.160	0.088 0.152	0.082 0.148	0.070 0.140
3	0.082 0.128	0.070 0.124	0.066 0.120	0.058 0.116

n is the number of experiments with the same set of tires. k is the number of experiments with different sets of tires of the same sort.

resistance. If, therefore, a number of tires of the same kind are tested in n different ways, then not only will the uncertainty of the test manifest itself but also the variation in the characteristics of the tires. This problem can be dealt with by the normal methods of test statistics and gives, for example, a number for the probable deviation of the mean obtained from the investigations with respect to the (unknown) true mean value.

Table 2 shows the influence of the variation coefficients of tire quality and test accuracy on the variation coefficients of the end result. If the tire quality is less constant, then more repetitions should be made with new pairs of tires.

The table gives calculated values for $V = \sqrt{\frac{V_1^2}{k} + \frac{V_0^2}{k \cdot n}}$. V_0 is the variation coefficient of wear of a tire. V_1 is the variation coefficient of the average wear of different tires of the same kind. The upper figures in each pair are based on the assumption: $V_1 = 0.10$, $V_0 = 0.10$. The lower figures are based on the assumption: $V_1 = 0.20$, $V_0 = 0.10$.

Finally the result of a wear experiment should always be translated for practical use into a sort of life expectancy. One criticism of the method of standardized tests of short duration is the question of the change of characteristics of the tread during the travel. To answer this question reference can be made to a number of studies in which the whole wear curve of a tire has been

determined. As a further answer we refer to our own experiments described in the following section, which demonstrate the absence of change of the relative wear resistance during the life under constant conditions.

RESULTS OF THE MEASUREMENTS

The first question we have studied in wear measurements is that of the relative wear resistance of natural rubber and synthetic rubber. By "synthetic rubber" is meant here the product of the American synthetic rubber industry which is currently the best suited for tire treads, namely cold GR-S or low-

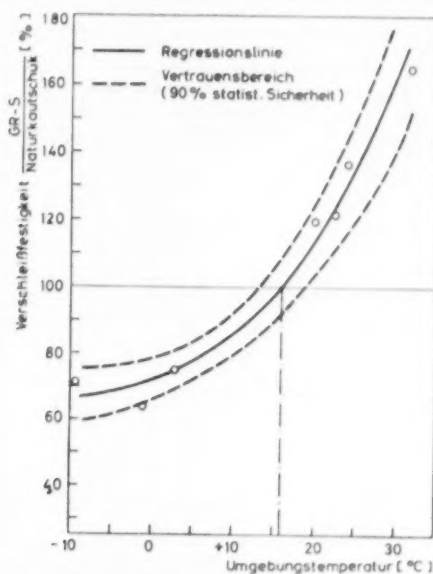


Fig. 2.—Relative wear resistance of GR-S and natural-rubber tire treads.

Ordinate: wear resistance $\frac{\text{GR-S}}{\text{Natural rubber}}$ (%).
 Abscissa: ambient temperature (°C).
 Regression line: ————
 Reliability range: - - - - -
 (90% statistical certainty)

temperature rubber. For testing relative wear resistance, tire treads were prepared from the two types of rubber compounded with HAF carbon black and other types of fillers according to a customary formulation. These tire treads, of which the details are given in Table 4, were vulcanized by recapping onto carcasses of normal fabric tires and then subjected to a series of tests in private passenger automobiles.

With Ford Mainline cars in the standardized wear tests, the relative wear resistance proved to be markedly dependent on the ambient temperature. If the wear resistance of cold GR-S was compared in each case with that of natural rubber, taken as 100, and if then the results were plotted as a function of the ambient temperature, the results shown in Figure 2 were obtained. The wear resistance figures for the two types of rubber were found to become

equal at about 15° C (60° F). Below 15° C natural rubber has better wear resistance than cold GR-S. The dashed curves in Figure 2 indicate the region within which, on the basis of these tests, the regression line should be found with 90 per cent statistical certainty.

It is most interesting to note that essentially the same results have been obtained by American workers. Various groups of American investigators have carried out wear measurements on automobiles in the years 1951 to 1954. These are summarized briefly in Figure 3. When it is considered that it is here a question of completely independent experiments made with very different methods, the agreement is certainly satisfactory. The striking thing is that

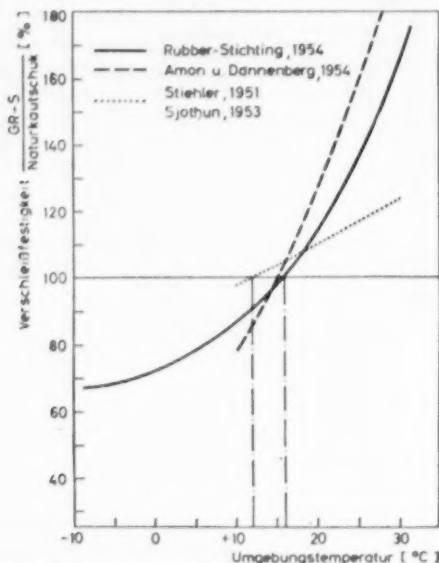


FIG. 3.—Relative wear resistance of GR-S and natural-rubber tire treads according to results of various investigators.

Ordinate: wear resistance $\frac{\text{GR-S}}{\text{Natural rubber}}$ (%)

Abcissa: ambient temperature (°C)

there are no American results below 12° C. This is probably because hitherto in the USA such measurements have usually been performed in Texas, where the winter temperature is about 12° C and the summer temperature about 30° C.

For calculations of the behavior of cold GR-S and natural-rubber tire treads in service, the regression line of Figure 2 could accordingly be used. To test this further, we have also undertaken wear measurements with non-standardized tests. Other vehicle types (Commer Truck R 762 and Renault-IV) and other travel routes were chosen. The tread surface profiles were also varied. These experiments are still in progress and their complete statistical evaluation is still lacking, but in Figure 4 the results that are already available are plotted, with account being taken of the reliability region for the wear resistance and the range of temperature variation of the ambient. In spite of the dispersion of the results, it is readily seen that no result deviates upward very much from

the regression line of the standardized experiments in Figure 2 and repeated in Figure 4.

Let us finally turn once more to the question of the life of the tire tread. It is impossible to make exact measurements of the absolute life, because too many variables come into play during the long periods. One should, therefore, decide upon an approximately specific value for the life and then use the much more accurately known relative wear resistance in order to compare the practical value of two tire types. In this case one must be certain that the relative wear resistance does not change during service. Actually there are experimental proofs that the relative wear resistance under unchanged conditions is

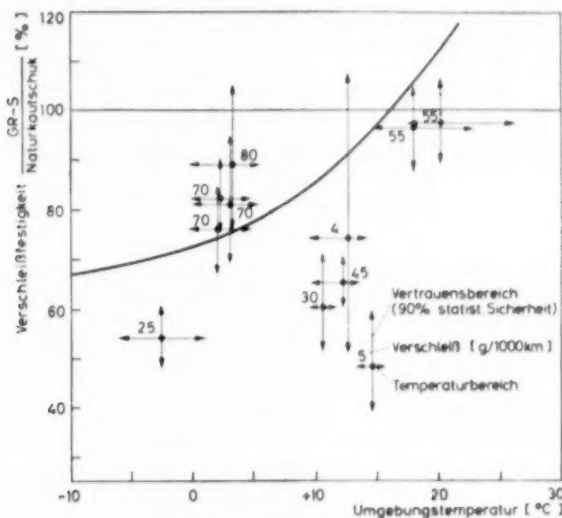


FIG. 4.—Relative wear resistance of GR-S and natural-rubber tire treads, taking into account the reliability range and ambient temperature.

Ordinate: wear resistance $\frac{\text{GR-S}}{\text{Natural rubber}}$ (%)

Abcissa: ambient temperature (°C)

On the diagram Vertrauensbereich (90% statist. Sicherheit) means reliability range (90% statistical certainty), Verschleiß (g/1000 km) means wear (g. per 1000 km.), and Temperaturbereich means temperature range.

constant throughout the whole life, provided that the first period (about 500 km. of normal use) is excluded (Buist, Stiehler). We found a further proof in the following series of tests. Four different tires were first "run in" on a Ford Mainline automobile for 500 km., then run to 2000 km. in a standardized experiment, then worn down on the race track until about 35 per cent of the tread surface was worn off, and finally tested again for 2000 km. in a standardized experiment. Simultaneously a similar set of four tires was tested in exactly the same way on another vehicle (Renault Frégate). There was very good agreement between the first and last measurement with both vehicles (Table 3), a further indication of the validity of our standardized tests for the determination of the relative life.

So far we have spoken only about measurements of private car tires, so the

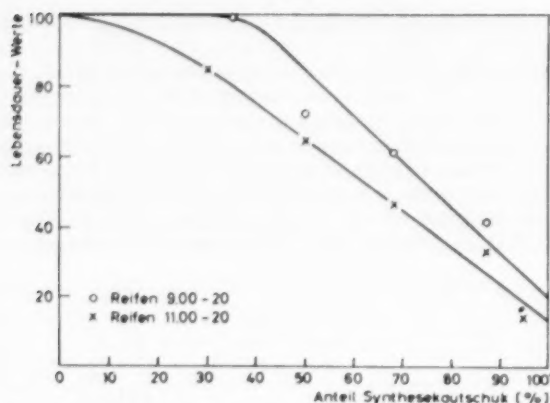


FIG. 5.—Life of truck tires (according to Rinne, Sjöthun, Greer, 1955).

Ordinate: Life values.
 Abscissa: Synthetic-rubber content (%).
 O Tires 9.00-20
 X Tires 11.00-20

question can be asked what the results would be in the case of truck tires. To be sure we have not been able to carry out many experiments on truck tires, but recent American work by Rinne, Sjöthun, and Greer may provisionally suffice to judge the relative results. These authors have compared truck tires of pure natural rubber with ones which contained 35, 50, 68, and 87 per cent GR-S. For practical reasons 100 per cent GR-S was not investigated. The results lead to two conclusions. The first is that here again in these experiments the relative wear resistance of natural rubber and cold GR-S depends more or less on the ambient temperature and that approximate equality is reached at 15° C. The second conclusion (see Figure 5) is that the addition of cold GR-S always leads to a shorter total life, because in truck tires the heat build-up of cold GR-S and the consequent destruction of the tire have a greater influence than the wear resistance. Our discussion of the advantages of natural rubber and cold GR-S treads must not for the present be extended to truck tires.

FUEL CONSUMPTION

FUEL CONSUMPTION AND ITS PRACTICAL SIGNIFICANCE

The combustion of fuel in a motor produces energy and heat. The energy, which forms only a fraction of the thermal value of the fuel, is used up in very

TABLE 3
 RELATIVE WEAR RESISTANCE $V \left(\frac{\text{GR-S}}{\text{NR}} \right)$ AND ITS RELIABILITY RANGE

(B_{90}) IN VARIOUS STAGES OF ABRASION

Ambient temperature 2°-3°C

Average speed 80 km. per hour

	After 8% abrasion	After 35% abrasion
Ford Mainline	$V = 78$; $B_{90} = 67 - 91$	$V = 79$; $B_{90} = 70 - 90$
Renault Frégatte	$V = 85$; $B_{90} = 68 - 106$	$V = 85$; $B_{90} = 68 - 106$

different ways. Acceleration of the vehicle, whether to increase the linear velocity, or to change the direction of travel in going around curves, requires only a small part of the energy. By far the greater portion serves to overcome frictional forces. One can distinguish between the friction of the vehicle with the surrounding air, friction in the drive, between moving parts, and friction of the tire surfaces on the road. What is often overlooked, however, is the friction in the interior of the tires when they are subjected to deformation.

When a piece of rubber is deformed, energy is expended, and in the ideal case this energy is completely regained with elastic retraction. Actually, however, this is not completely the case. Instead, part of the energy is lost in the form of internal friction, and the extent of this loss depends on the characteristic properties of the rubber. The non-recoverable part is called *hysteresis loss*, and obviously the fuel is expended in this hysteresis loss in the tires, and like other frictional losses, this loss must also be reduced as far as possible for economical driving.

Now it is known that cold GR-S vulcanizates show considerably greater hysteresis losses than the corresponding natural-rubber vulcanizates, so in any comparison of the economy of cold GR-S and natural rubber tires, this point should not be overlooked.

MEASUREMENT OF FUEL CONSUMPTION

The measurement of fuel consumption in an automobile has often been described in the technical literature. When, however, the above mentioned groups of factors, which all combine to determine the fuel consumption are taken into consideration, it becomes evident that comparative measurements of cold GR-S and natural-rubber tires place very high demands on the accuracy required. Because of the great influence of every acceleration, only by measurements under steady operating conditions is it possible to detect any differences.

The experiment was arranged as follows. A private automobile (Ford Mainline) with natural-rubber tires travels back and forth over a fixed 10 km. stretch of an automobile road. After the car has travelled for a sufficient time at the prescribed speed, all temperatures become constant and measurements are begun. With travel in one direction, the distance which has been traveled with the amount of fuel contained in a buret is determined about six times. Both during the measurements and over the stretches of road in between, the speed is held constant at the prescribed rate. The distance per buret capacity is about 1 km., and this is determined by means of an exactly calibrated very light "fifth wheel". These six observations of travel in one direction are now followed by six similar ones in the opposite direction. The whole experiment is then repeated once or twice more. Immediately following this, the four natural-rubber tires are replaced with similar GR-S tires and the same experiment is repeated several times with these tires. Finally a series of measurements is made with the four natural-rubber tires. The whole program just described furnishes *one observation*. The wind velocity and the road traffic are the most important disturbing factors. For this reason measurements are usually made at night.

Repetitions at the same speed or at other speeds and ambient temperatures provide further observations.

If there is no particular need for measuring the actual fuel consumption in service, other methods can be used. In particular, comparative measurements

of the rolling friction of the two types can be made. The rolling friction can be determined mechanically under standardized conditions by means of a special apparatus, and it is directly related to the fuel consumption.

NATURE, ACCURACY, AND SIGNIFICANCE OF FUEL CONSUMPTION MEASUREMENTS

From what has been said the significance of fuel consumption measurements can be directly deduced. The objection might be raised that our results apply only to steady operating conditions and not to extremely variable conditions of service. However, it must be realized that the steady state condition is a necessary one for making the measurement, but that on the other hand the measured differences in hysteresis loss of the two types of tires will still hold

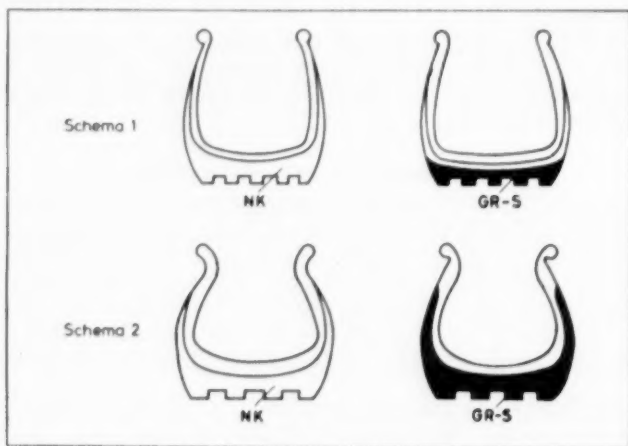


Fig. 6.—Difference in fuel consumption (ΔT) of cold GR-S and natural rubber.

Ambient temperature: 10°–17° C (Scheme 1).

12°–27° C (Scheme 2).

Travel speed: 46–80 km. per hour.

Tire pressure: about 2.00 kg. per sq. cm.

ΔT Scheme 1; mean value 1.7%; reliability range (90%) 0.8–2.6%.

ΔT Scheme 2; mean value 3.3%; reliability range (90%) 2.7–3.9%.

even under non-steady operating conditions. In this measurement the travel is made alternately with two sets of tires, and it is absolutely essential that the conditions be the same for both. The steady state condition is so well defined that it is reproducible, whereas non-stationary states are not.

The accuracy of the observations is satisfactory because of the large number of measured values. The results represented in Figure 6 give an average value with a reliability range (for 90 per cent statistical certainty) of 0.8 to 2.6 per cent and 2.7 to 3.9 per cent, respectively. Every observation is based on at least 24 measurements on the one type of rubber and 48 on the other.

It is interesting that the observations for speeds between 40 and 90 km. per hour and for ambient temperatures do not show any systematic influence. Nevertheless, in case there is such an influence, it is so small as not to be measurable on account of the disturbing influence of wind and traffic.

RESULTS OF MEASUREMENTS

Two important series of observations were made. The first series relates to tires which differed only in the actual tread surfaces (soles). The two sets of four tires consisted of natural rubber with the exception of the tread surfaces of one set made with cold GR-S. The soles of natural rubber or cold GR-S were bonded by recapping onto finished new tires. Formulation and preparation are given in Table 4. The difference in fuel consumption here amounted to about 1.7 per cent.

In the second series the two sets differed not only in the tread surfaces but also in the side walls, which in one case likewise consisted of GR-S. The tires in this second series were new throughout, i.e., not retreaded. The difference in fuel consumption here was 3.3 per cent. The side walls obviously have a considerable influence. The absence of any influence of ambient temperature and speed have already been pointed out. Our results are in agreement with earlier ones of Evans (1948).

TABLE 4
COMPOUND FORMULAS OF THE TIRE TREADS
(TIRE DIMENSIONS 6.70×15)

	Tread		Tread and sidewall	
Smoked sheet rubber (RSS No. 1)	100		100	
Polysar Krylene ("cold rubber")		100		100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Sulfur	2.5	2	2.5	2
Santocure	0.6	1.6	0.55	1.2
Di- <i>o</i> -tolylguanidine	—	—	—	0.4
Phenyl-2-naphthylamine	1	1	1	1
Vultrol	0.5	—	0.5	—
Dutrex-55	3	5	3	5
Vulcan-3 (HAF)	50	50	45	45
Preparation	Recapping		New	New
Vulcanization	60 min. at 150° C		30 min. at 130° C	

A further confirmation has been obtained by us in a joint study with the Union Technique de l'Automobile, du Motocyclette, et du Cyclette (U.T.A.C.) in Paris. In measurements of the rolling friction by means of a special apparatus, a difference of about 13 per cent was found between natural-rubber treads and cold GR-S treads. This difference relates to the treads applied by us by recapping. It is seen that the difference in rolling friction amounts to about six times the difference in fuel consumption. This arises from the fact that only one sixth of the motive energy is consumed in overcoming the rolling friction of the tire. A corresponding correlation was also found by Evans in the difference between fuel consumption and rolling friction.

CONCLUSIONS

In order to survey the economics for a given country of driving with cold GR-S and natural-rubber tires, we proceeded as follows.

With the usual average life of a tire as a starting point, the difference in life was calculated for the two types of rubber on the basis of relative wear resistance measurements. Based on the price of the tire this difference at each

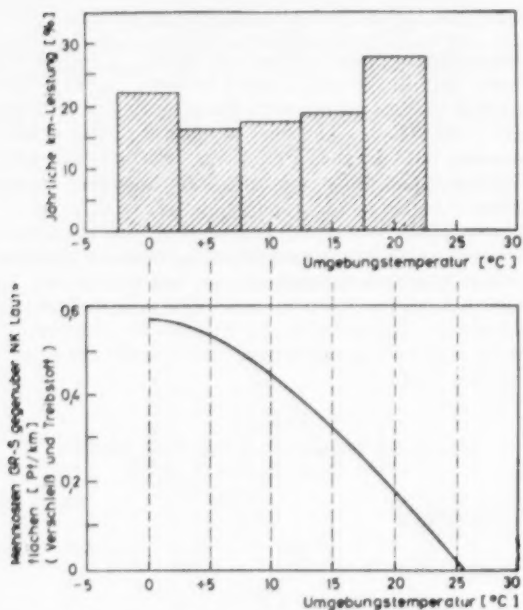


FIG. 7.—Economics of truck tires in West Germany. Excess cost of GR-S over natural-rubber treads (pfennig per km.) (wear and fuel) vs. ambient temperature.

Upper ordinate: Yearly km. performance (%).

Lower ordinate: Excess cost (pfennig per km.) of GR-S vs. natural-rubber treads. (Wear and fuel consumption.)

Both abscissas: ambient temperature ($^{\circ}\text{C}$).

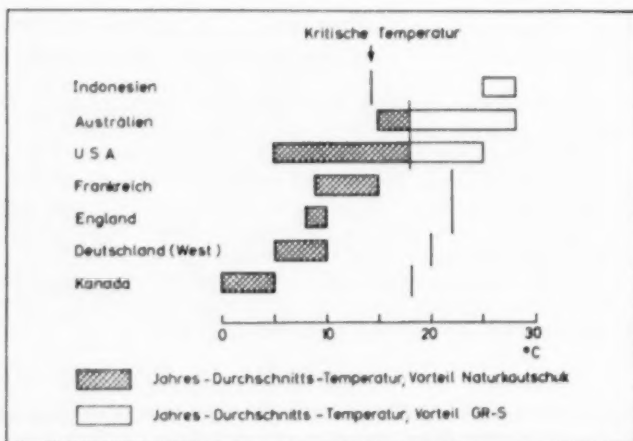


FIG. 8.—Natural and GR-S treads in various countries. The crosshatched blocks indicate the average annual temperature range where natural rubber is superior; the plain block the average annual temperature where GR-S is superior. The vertical arrow indicates the critical temperature. The countries are in descending order: Indonesia, Australia, United States, France, Britain, West Germany, and Canada.

temperature is expressed in terms of money. There is obtained in this way, therefore, for the country selected, a curve showing price difference vs. temperature. This curve has to be further corrected because of the greater fuel consumption when the driving is done with cold GR-S tires. Even with equal tire life, it is certainly an advantage to save some fuel. Since our observations on fuel consumption showed no dependence on temperature, this correction only produces a parallel displacement of the curve of price difference vs. temperature. As an example, the resulting curve for West Germany is given in Figure 7 (lower diagram). With the aid of this curve every car driver in West Germany can calculate for himself what is the advantage or disadvantage of natural-rubber tires. For this he needs only to know how many kilometers he has gone at the different temperatures.

The upper half of Figure 7 gives a view of the distribution of kilometer performance (mileage) of all private cars in West Germany. The percentage of the tire mileage at the different temperatures is given. In deriving these results, use was made of some statistical data on the traffic density in different months of the year. These data were from the Central Bureau voor de Statistiek in the Hague. Also the meteorological mean temperature values for definite hours of the day and months of the year were taken into account.

The conclusion for West Germany is that, on the average, there is a distinct advantage in driving with natural-rubber tires. Conclusions for other countries can be drawn in a similar manner. They are given in very brief form in Figure 8.

Surprisingly enough Figure 8 shows that GR-S is advantageous only in a very warm, i.e., tropical, climate. In all other countries, natural rubber shows more or less advantage. An estimate by J. C. Gerritsen, to whom we also are indebted for most of the preceding calculations, shows that over 70 per cent of the motor vehicles in the world can run more economically on natural-rubber tires.

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THE STRUCTURE OF CRYSTALLINE 1,2-POLYBUTADIENE AND OF OTHER SYNDYOTACTIC POLYMERS *

G. NATTA AND P. CORRADINI

ISTITUTO DI CHIMICA INDUSTRIALE DEL POLITECNICO DI MILANO, ITALY

INTRODUCTION

Systematic x-ray and electron diffraction studies of polymers of 1,3-butadiene prepared by different anionic catalysts have made it possible for us to identify two types of highly crystalline materials. One of us (G. N.) has already reported that our synthesis was carried out with the aid of different highly selective catalysts. The description of the preparation of these catalysts, which have made it possible for the first time to prepare these new polymers, will be separately published by one of us (G. N.) with L. Porri.

Infrared analysis carried out by E. Mantica and D. Morero in our Institute has established that one type of these crystalline polymers obtained with heterogeneous catalysts represents a continuous 1,4-*trans* arrangement of the monomer units. X-ray diffraction has shown that this material is dimorphous, having one crystalline modification that is stable at room temperature and another stable above 60° C. The x-ray melting point of a polymer having a molecular weight of the order of 100,000 is around 130° C.

The low-temperature modification has an identity period of 4.9 Å along the chain axis and a hexagonal packing with a period of $a = 4.54$ Å perpendicular thereto, but the symmetry of the crystals, as a whole, is lower. The high temperature modification seems to have the chains in helicoid form.

The other crystalline polymer consists essentially of 1,2-monomer units; infrared studies have shown that more than 90 per cent of its double bonds are of the vinyl type and the residual 10 per cent represents a mixture of *cis* and *trans*. The higher the proportion of 1,2-units, the more crystalline is the material. Figure 1 shows the infrared absorption curves of two different typical samples of the product.

In this article, we limit ourselves to describing the structure of the latter polymer, which, in our opinion, is the more interesting material and which we shall simply call 1,2-polybutadiene. We shall report on the structure of the two modifications of the 1,4-*trans*-polybutadiene in another paper together with the study of the structure of other crystalline polydienes.

The 1,2-polybutadiene to be described represents the first high melting (about 150° C), highly crystalline polymer of butadiene that is linear and non-rubbery. Its melting point is higher than that of isotactic polybutylene (125–130° C) and very close to that of isotactic polypropylene (160–170° C)², which is in accord with the greater stiffness of the $-\text{CH}=\text{CH}_2$ group compared with $-\text{CH}_2-\text{CH}_3$. Of equal interest is the fact that the 1,2-polybutadiene is the

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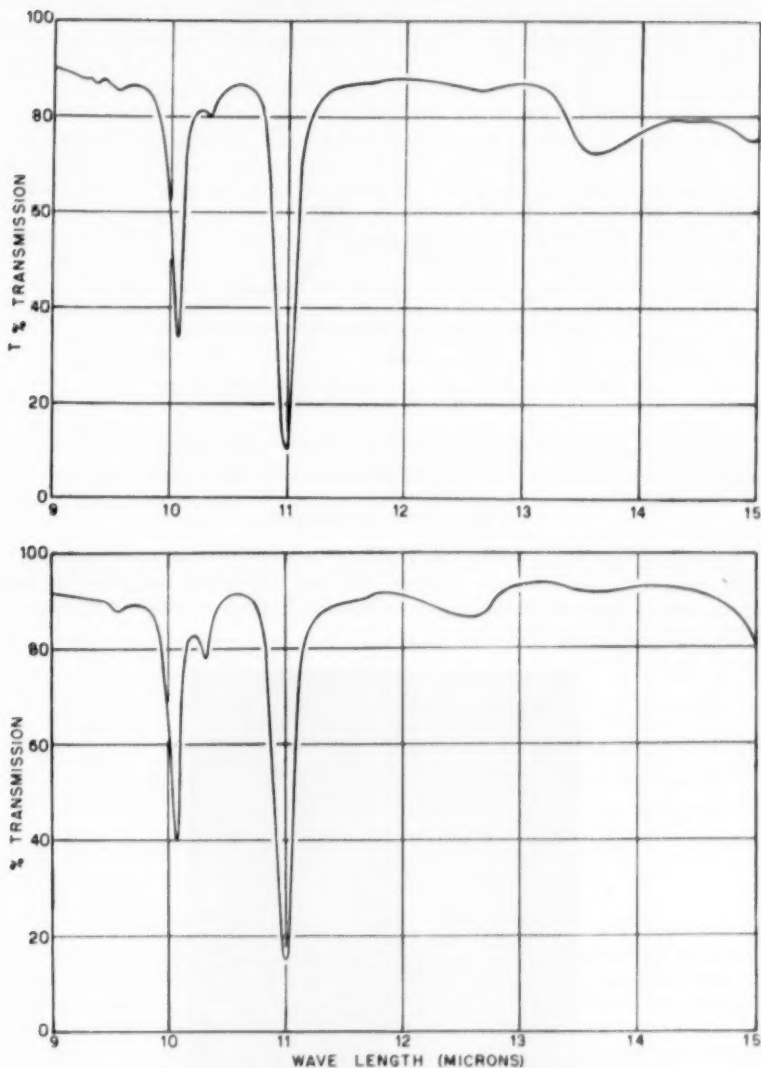


Fig. 1.—Infrared absorption spectra of 1,2-polybutadiene.

first case of a vinyl type of polymer, ($\text{CH}_2\text{-CHR}$), that is highly crystalline but not isotactic. Indications of imperfect crystallinity have already been reported for a few known polyvinyl derivatives of nonisotactic character such as stretched fibers of polyvinyl chloride prepared with the aid of free radicals as initiators⁵. The few and not sharp x-ray diffraction spots given by these materials were correlated with the presence of a planar zigzag chain, with the substituents alternating in *D*- and *L*-configuration with respect to the plane of the

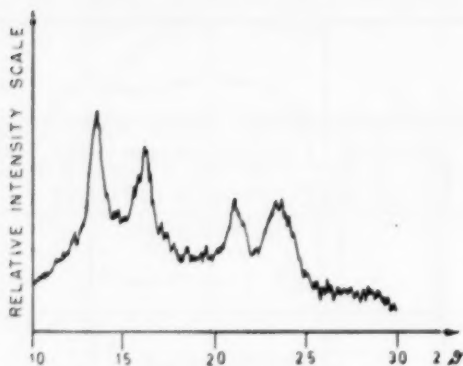


FIG. 2.—Geiger counter registration curve of the reflections of 1,2-polybutadiene with $\text{CuK}\alpha$ radiation.

zigzag. The absence of sharp and well-developed fiber diagrams did not make possible a very profound study of the structural details of these materials.

X-RAY INVESTIGATION

1,2-Polybutadiene, a white easily moldable powder, was investigated with $\text{CuK}\alpha$ radiation and a Geiger counter; it gives diffraction maxima distinctly different from those of isotactic poly- α -butylene²; they correspond to spacings of 6.60, 5.49, 4.20, and 3.80 Å.



FIG. 3.—X-ray fiber diagram of 1,2-polybutadiene.

The diffraction line of 3.80 Å does not appear in samples that are molded at low temperatures in such a manner that a planar orientation is developed; this spacing therefore belongs to a set of planes, the last index of which is different from zero². In fact, a rodlet of the polymer extended at high temperatures and cold-drawn produces a fiber diagram in which the first three reflections appear on the equator (Figure 3), whereas the 3.80 Å spot falls on the first layer line. The identity period along the fiber axis is 5.1 ± 0.1 Å.

The powder diagram was obtained in a camera capable of operating at different temperatures and described elsewhere². It was found from the disappearance of the diffraction lines that the material fuses completely at 154° C. The temperature spread, which is shown in Figure 4, corresponds to the normal behavior of high polymers and can only partly be attributed to the presence of monomer units in different configurations which form amorphous areas.

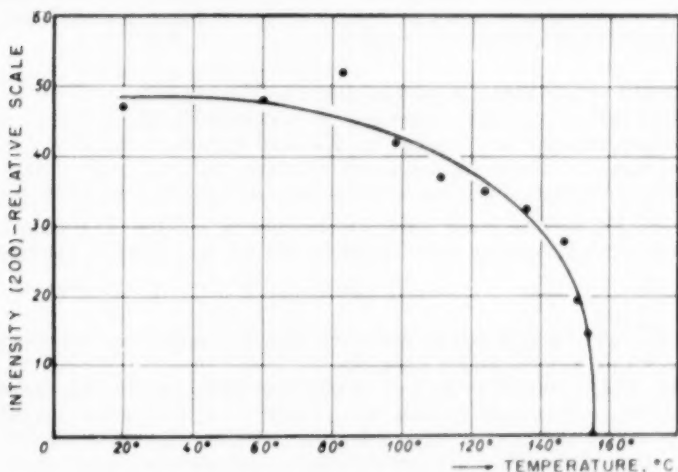


FIG. 4.—Melting point curve of 1,2-polybutadiene taken with x-rays.

ELECTRON DIFFRACTION STUDIES

We have already observed with other polymers that in many cases it is advantageous to study the diffraction of electrons by thin layers of polymers, because in such thin films the polymer molecules tend to assume a preferred orientation spontaneously. Also with crystalline 1,2-polybutadiene, electron diffraction studies have proved to be very useful. Very thin layers (about 100 Å thick) of the polymer were made by evaporation of a benzene solution on water and showed all the polymer molecules to be oriented with their axes perpendicular to the plane of the layer. These films were examined on a copper screen with a Finch electron diffraction camera in cooperation with I. W. Bassi.

INTERPRETATION OF THE DIAGRAMS

The transmission diagrams obtained with electrons can be considered as a direct representation of a section of the reciprocal lattice by a plane passing through its origin. In our special case, where the crystallites are very small

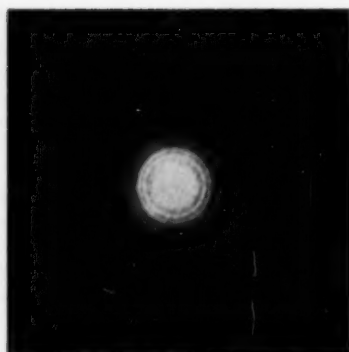


FIG. 5.—Electron diffraction diagram of a thin film of 1,2-polybutadiene beam perpendicular to plane of film.

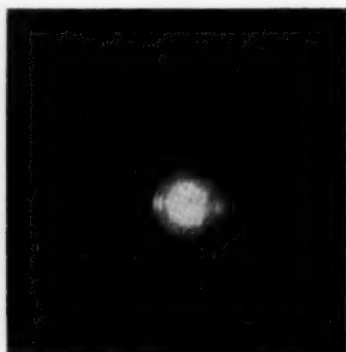


FIG. 6.—Same diagram with oblique irradiation.

and parallel to a crystallographic direction c (coinciding with c^*), the set of their reciprocal lattices is given by concentric circles formed by the intersection with planes perpendicular to c (spaced by $1/c$) and cylinders coaxial to c with a radius $1:d(hk0)$. If one irradiates a thin film perpendicular to its surface with electrons, the reflection plane cuts the reciprocal lattice in a set of circles with radii $1:d(hk0)$, because a and b are perpendicular to c . The diagram contains only reflections indexed by $(hk0)$, which form a set of circles with the radii r

$$r = \lambda R/d(hk0)$$

where λ = wave length and R = distance between sample and photographic plate. Figure 5 shows such a diagram.

If the film is rotated by an angle δ with respect to the previous position so that its plane is then inclined to the beam at $(90^\circ - \delta)$, the reflection plane then cuts the reciprocal lattice at points falling on parallel straight lines which are the intersections of the reflection plane with reciprocal lattice planes distanced from each other by $1/c$. The distance between these straight lines is $\lambda R/c \sin \delta$. Each reflection also falls on a circle of the radius $\lambda R/d(hkl)$. Figure 6 shows a pattern of this type and Table I the figures obtained from it.

The equatorial reflections (Figure 7) can all be explained on the basis of a plane rectangular lattice, with $a = 10.98 \pm 0.10$ Å and $b = 6.60 \pm 0.05$ Å.

TABLE I
 $\lambda R = 5.435 \times 10^{-8}$ cm.²

Equator		First layer line	
$2r$ (mm.)	Intensity	$2r$ (mm.)	Intensity
8.3	<i>s</i>	14.3	<i>s</i>
9.9	<i>s</i>	19.9	<i>w</i>
12.9	<i>s</i>	28.2	<i>w</i>
16.9	<i>ms</i>		
19.2	<i>mw</i>	23.2	<i>ms</i>
21.4	<i>m</i>	27.3	<i>mw</i>
25.8	<i>m</i>	28.6	<i>ww</i>
29.5	<i>w</i>	30.7	<i>w</i>
30.7	<i>w</i>	32.9	<i>mw</i>

In order to index the higher layer lines, we have used the construction indicated in Figure 7. On the line OP we plot, beginning at O , segments $OP(hk0)$, which are proportional to all possible values of $1:d(hk0)$. One does the same on the parallel line $O'P'$, $O''P''$, which are drawn at distances proportional to $1/c$. If the lattice is orthorhombic, the circles with radii proportional to $1:d(hkl)$ and with the center in O will intersect the line $O'P'$ with $l = 1$, $O''P''$ when $l = 2$ at points $P'(hk1)$ or $P''(hk2)$, respectively, which give us the indexes of the reflections. Figure 7 shows that this construction can be applied successfully in our case.

The best evaluation leads to an elementary cell with $a = 10.98$ Å, $b = 6.60$ Å, and $c = 5.14$ Å. The theoretical density (assuming four monomers in the cell) is 0.963. This must always be higher than the experimental value (0.92) because of the presence of less dense amorphous areas.

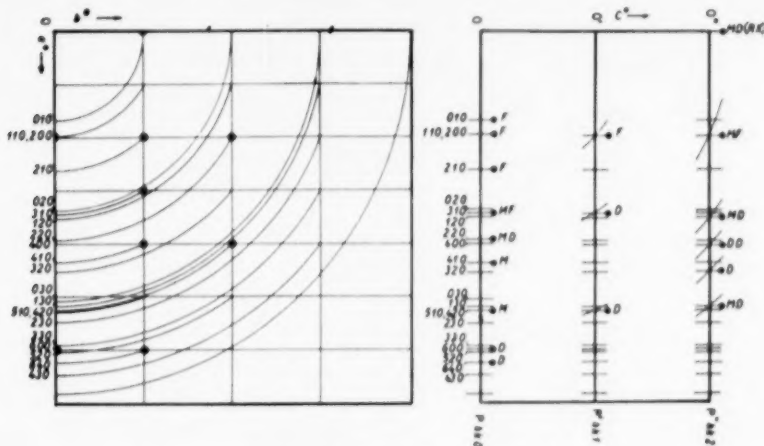


Fig. 7.—Reconstruction of the reciprocal lattice of 1,2-polybutadiene.

The absence of reflections $0kl$, for $l = 2n + 1$ and $h0l$ for $h = 2n + 1$, which may not be completely conclusive because of possible very small intensities, and considerations of packing possibilities of the molecules indicate $Pacm$ as the most probable space group.

DETERMINATION OF THE STRUCTURE

For simplicity we shall denote by C_1 and C_2 the carbon atoms CH_2 and CH in the main chain and by C_3 and C_4 the carbon atoms CH and CH_2 of the pendent vinyl groups. The general weakness of the $hk0$ reflections with $h = 2n$ affirms the fact that atoms C_1 and C_2 of the main chain are projected along c in the neighborhood of $x = 0, y = 0$ and $x = 1/2, y = 0$. The identity period of 5.1 Å parallel to the fiber axis coincides with the presence of a plane rigid zigzag paraffin chain, with a periodicity represented by four carbon atoms. Since this identity period corresponds to two monomer units, one must conclude that the two vinyl groups alternate in opposite positions, as if they were attached to two asymmetric carbon atoms that have the L - and D -configuration, respectively. Such a distribution has been proposed to explain the diffuse scattering of poly-

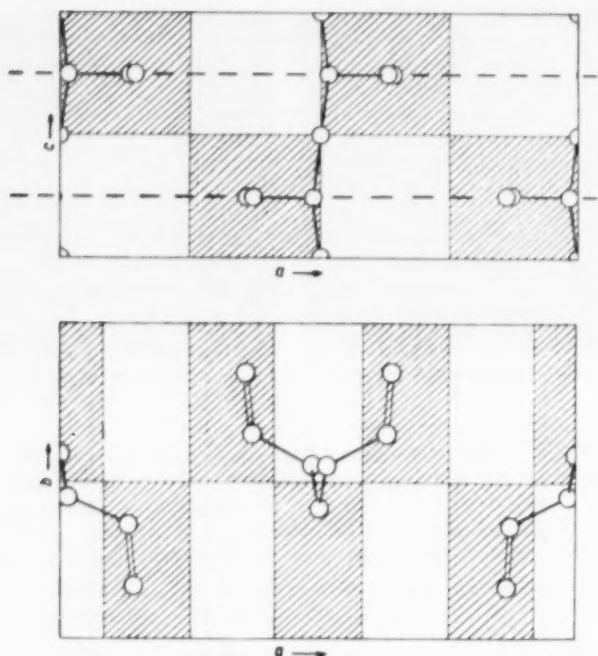


FIG. 8.—Negative and positive areas of the structure factors of the reflections (201) and (310).

vinyl chloride, although the diagrams of this material reveal a much lower degree of order than in the present case.

From the space group *Pacm* it follows that the molecule itself has a plane of symmetry with a translation period of $1/2$ along c . The plane paraffin chains therefore lie in the planes $(0, y, z)$. Assuming now a certain chain model in concordance with these conditions, it is possible to localize the molecules in the cell and to calculate the structure factors with only one variable parameter along direction b . In order to localize the vinyl groups in a tentative fashion, one is guided by the exceptional intensity of the (201) reflection, which indicates that these groups alternate in the *D*- and *L*-configuration, changing from one into the other with respect to the adjacent molecules as one proceeds one-half of the identity period along c (see Figure 8). Equally important is the high intensity of (310) independent of the reflectivity of the chain carbon atoms because $h = 3$ and therefore probably mainly caused by the arrangements of the vinyl groups (see Figure 8).

In the calculation of the structure factors, we have assumed the atomic distances and valence angles as generally accepted and found that a model with a planar paraffin chain parallel to $(0, y, z)$ and with the coordinates:

	x	y	z
C_1	0	0.896	0
C_2	0	0.030	0.250
C_3	0.117	0.164	0.250
C_4	0.117	0.364	0.250

gave the best agreement between experimental and calculated intensities (see Table II). This model, as any other model in which the chains are planar, leads, however, to a crowding of the atoms C_1 and C_4 (3.9 Å) and also to a rather close approach of the C_4 atoms of the same chain, which appears to be excessive in view of the distances between the other carbon atoms (ca. 4.2 Å) of the model.

We have, therefore, examined other models in the same space groups by making slight adjustments of the above coordinates, abandoning the complete planarity of the backbone chain. One arrives at a better agreement and at a better packing of the molecules by a model not much different from the above,

TABLE II
ATOM FORM FACTORS TAKEN FROM X-RAYS

Indexes	nF^2 (first approach)	nF^2 (final approach)	Intensity
010	64	90	<i>s</i>
110, 200	136	87	<i>s</i>
210	116	116	<i>s</i>
020	5	6	—
310	50	67	<i>ms</i>
120	12	1	—
220	26	42	<i>mw</i>
400	—	0	—
410	65	46	<i>m</i>
320	4	2	—
030	1	4	—
130	0	0	—
420, 510	96	58	<i>m</i>
230	1	3	—
330	6	6	—
600	12	49	<i>w</i>
520	3	4	—
610	34	27	<i>w</i>
111, 201	96	131	<i>s</i>
211	0	2	—
311	39	19	<i>w</i>
121	0	0	—
221	7	4	—
401	1	1	—
411	1	3	—
321	0	2	—
131	2	3	—
421	0	3	—
511	8	24	<i>w</i>
231	0	0	—
331	3	3	—
002	20	20	<i>mw</i> (x-ray)
012	0	1	—
112, 202	72	59	<i>ms</i>
212	0	0	—
022	0	1	—
312	0	3	—
122	23	30	<i>mw</i>
222	4	2	—
402	25	22	<i>ww</i>
412	1	0	—
322	21	24	<i>w</i>
032	5	2	—
132, 422	52	52	<i>mw</i>
512	3	1	—
232	8	2	—

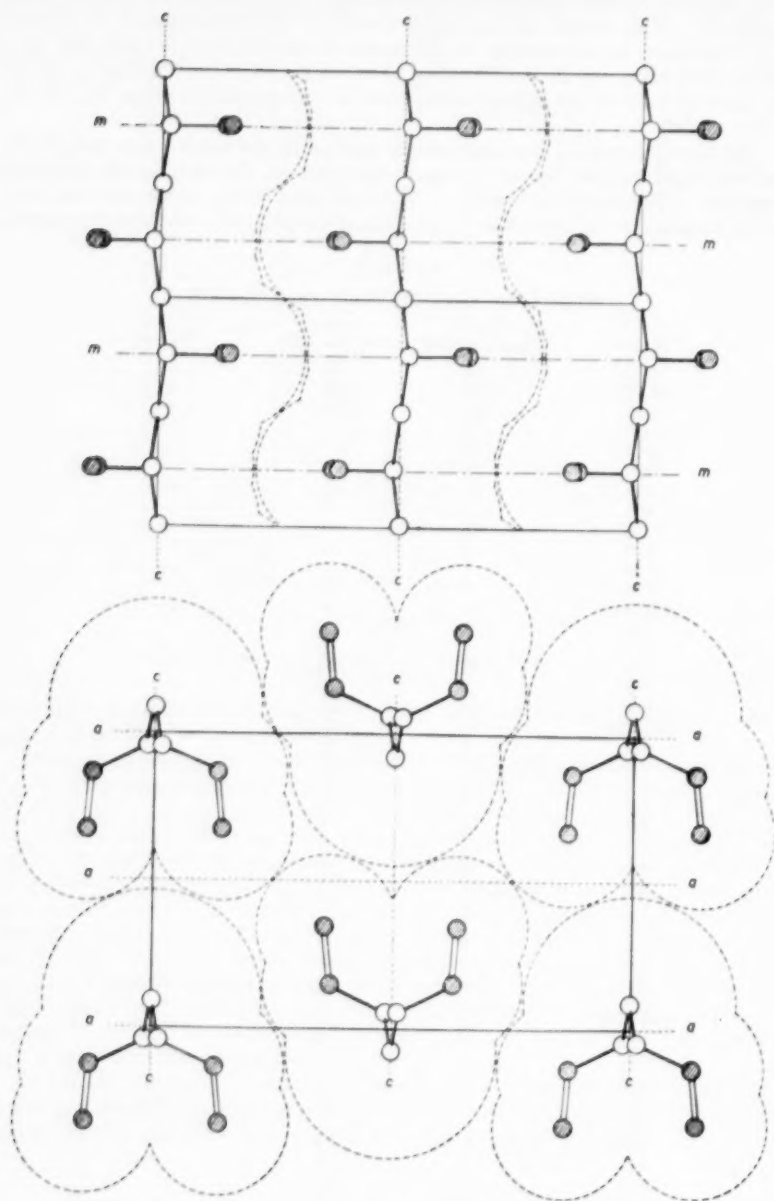


FIG. 9.—Model of the structure of 1,2-polybutadiene.

TABLE III

VAN DER WAALS' DISTANCES BETWEEN C-ATOMS OF DIFFERENT CHAINS FOR THE SECOND MODEL

$C_4 \dots C_4$	4.0 A.
$C_4 \dots C_1$	4.3-4.4 A.
$C_2 \dots C_3$	4.0 A.
$C_2 \dots C_1$	4.2 A.
$C_4 \dots C_4$ (same chain)	4.0 A.

in which the chains are somewhat nonplanar. It is shown in Figure 9, and its coordinates are :

	x	y	z
C_1	0	0.916	0
C_2	0.014	0.050	0.250
C_3	0.136	0.143	0.250
C_4	0.143	0.342	0.250

Table II shows a comparison of the experimental intensities with the F^2 -values computed for the two models. The van der Waals' distances between carbon atoms of different chains corresponding to the second model are all equal to or larger than 4.0 Å and are given in Table III.

The calculated structure factors favor to a slight extent the second model, but only a more detailed structure investigation (probably only with the aid of better x-ray diagrams) can finally settle this question.

The valence angles:



in the main chains are 113° , in good agreement with other reported values⁴, such as polyethylene (111°), polypropylene (114°), polyisobutylene (114°), and polystyrene (116°).

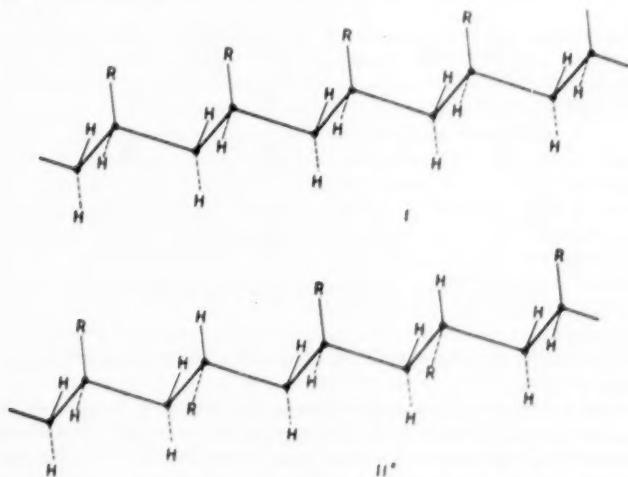


FIG. 10.—Models of isotactic (I) and syndiotactic (II) structure with planar chains.

DEFINITION OF SYNDYOTACTIC POLYMERS

The structure of 1,2-polybutadiene as described in the preceding paragraph merits a special discussion of its characteristics. It is the first case of a polyvinyl derivative in which a regular alternation of the *D*- and *L*-configuration of the substituents has been established, and also is the first case of a polyhydrocarbon of high molecular weight combining asymmetric carbon atoms with a relatively large substituent which is crystalline, and the chain of which is essentially planar. It may, therefore, be interesting to compare this structure with

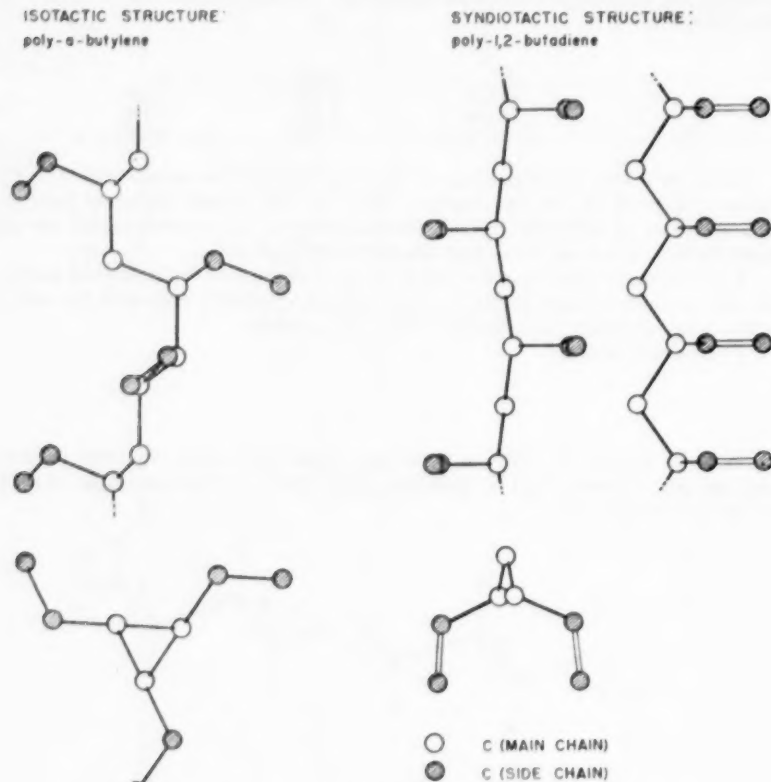


FIG. 11.—Models of 1,2-polybutadiene and poly- α -butylene.

that of crystalline polyolefins which show simply a regular succession of tertiary carbon atoms with the same steric configuration alternating with CH_2 groups in the main chains.

In a paper presented to the Accademia dei Lincei² in December, 1954, we defined as isotactic polymers those linear crystallizable polymers of alpha olefins of head-to-tail structure in which, over a certain chain length, the asymmetric carbon atoms display the same steric configuration. These materials have high melting points and possess in the crystalline state helicoid chains that are quite different from those found in 1,2-polybutadiene (lower structure

in Figure 10). This structure differs rather noticeably from that of an isotactic polymer such as poly- α -butylene, in that, if the main chain of the latter were completely accommodated in one plane, the substituents R would be all above or all below that plane (upper structure in Figure 10).

In reality, because of the steric interference of the C_2H_5 groups with each other, the main chain of poly- α -butylene cannot possess a planar structure and does assume the helicoid configuration described in an earlier paper, whereas in the 1,2-polybutadiene a certain degree of planarity is possible for the main chain because of the more favorable arrangement of the vinyl groups. The difference between the two structures becomes more evident if one examines the projections of the main chains on two planes—one perpendicular to and one parallel with the axis of the molecule (Figure 11). Both types of chains represent a high regularity but, whereas isotactic chains have—over a certain length—all asymmetric carbon atoms in the same configuration, the chains of 1,2-polybutadiene are characterized by a regular alternation of D- and L-configurations along the length of the chains.

TABLE IV
LATTICE SPACINGS OF POLYVINYL CHLORIDE

Indexes	d (experimental), Å	d (theoretical), Å
200}	5.39	5.4
010}		5.3
110	4.78	4.79
210	3.74	3.76
310	2.94	2.95

We propose to call all vinyl polymers with alternating D- and L-configurations of their substituents (like 1,2-polybutadiene) *syndiotactic polymers*, using the Greek words *tatto* (put in order) and *syndyo* (every two).

STRUCTURE OF POLYVINYL CHLORIDE

In connection with our results on the structure of 1,2-polybutadiene, we have resumed the study of the x-ray diagrams given by other polyvinyl compounds of equal identity period, such as polyvinyl chloride, to find out whether they also possess a syndiotactic structure. Previously their imperfect crystallinity did not make possible sufficiently thorough investigation.

Oriented fibers of polyvinyl chloride, prepared with the aid of free radical catalysts, give an x-ray diagram with imperfect layer lines, indicating the existence of laterally ordered domains (about 50 Å wide) with a rather poor order along the length of the chains. The diagram reveals equatorial reflections with $d = 5.39, 4.78, 3.74$, and 2.94 Å. These values, observed by us, are in agreement with those reported in literature⁵. The first, very diffuse, layer line has a maximum at $d_{eq} = 5.3$ Å; the identity along the fiber axis is 5.1 ± 0.1 Å.

Assuming that polyvinyl chloride crystallizes in the orthorhombic space group $Pacm$ and that the arrangement of the macromolecules is similar to that of 1,2-polybutadiene, one can interpret all equatorial reflections by an orthorhombic cell with the axes $a = 10.6 \pm 0.1$, $b = 5.4 \pm 0.1$ Å.

In Table IV the experimental and theoretical spacings of five planes are compared.

The four strongest reflections of 1,2-polybutadiene have the same indexes: 010, 200 + 110, 210, and 310.

TABLE V
EXPERIMENTAL AND THEORETICAL INTENSITIES OF POLYVINYLCHLORIDE

Indexes	<i>d</i> , Å	Intensity (measured)	<i>F</i> ² (calculated)
200	5.39	<i>m</i>	60
010	—	—	—
110	4.74	<i>m</i>	55
210	3.74	<i>w</i>	21
310	2.94	<i>w</i>	18
All other intensities			<<10

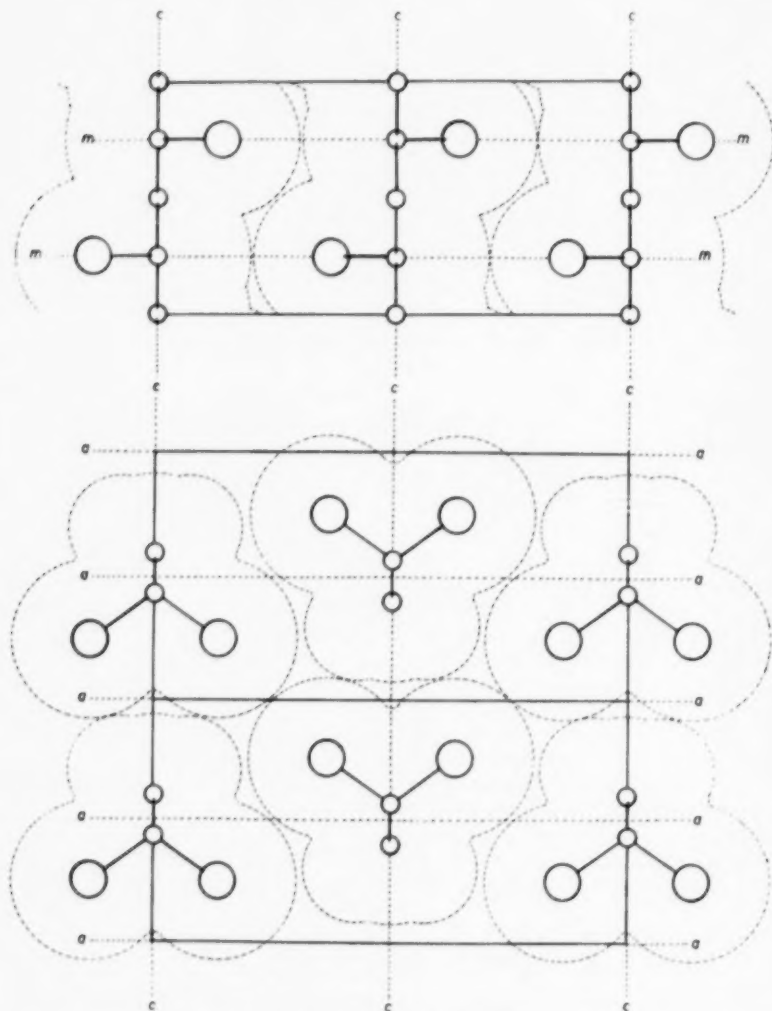


FIG. 12.—Model of the structure of polyvinyl chloride.

The x-ray density of polyvinyl chloride is calculated to be 1.44, in good agreement with the experimental values (1.39–1.41).

Calculating the structure factor with the coordinates:

	<i>x</i>	<i>y</i>	<i>z</i>
C(H ₂)	0.25	0.107	0
C(H)	0.25	0.066	0.25
Cl	0.134	0.25	0.25

one arrives at good agreement with the experimental intensities if one uses a temperature factor $B = 20 \times 10^{-16} \text{ cm}^2$, which one might better call here a factor of lateral disorder. Table V gives the results of this calculation.

The model represented in Figure 12 corresponds to a planar chain. Any deviation from planarity greater than 5° of the type found in the polybutadiene would lead to a discrepancy between observed and calculated intensities.

The arrangement of the molecules parallel to *a* leads to a close packing of the Cl atoms of 4.4 Å, in agreement with the minimum distances of 4.2 to 4.3 Å found in other organic structures; the distribution along *b* is determined by an approach between Cl and CH₂ of 3.93 Å in accord with corresponding minimum values of 3.65 in other organic structures (see Figure 12). Also, the intensities along the layer lines are in agreement with the postulated structure; the maximum on the first layer line corresponds to (201), which is an intense reflection in the pattern of 1,2-polybutadiene. The lack of order along the *c*-axis can be attributed to imperfections in the syndiotactic arrangement of the Cl atoms. The syndiotactic segments of the chains arrange themselves through orientation in crystalline areas that are relatively extended along *a* and *b* but are only rather short in parallel to the *c*-axis.

These imperfections must be caused by the fact that the polyvinyl chloride samples were prepared with free radical initiators and hence by a less regular polymerization process which is exposed to perturbations by chain transfer and by head-to-tail versus head-to-head addition. It is possible also that during the addition of any individual monomer to the growing chain the two possible configurations, D and L, alternate with each other in a statistical manner. Whatever the reason for the imperfections may be, it is justified to assume also in this case the existence of short segments with syndiotactic structure.

SYNOPSIS

With the aid of anionic polymerization catalysts, 1,2-polybutadiene of high molecular weight has been synthesized. It is a crystalline material with a melting point above 150°C . Electron and x-ray diffraction studies with oriented films made possible determinations of the elementary cell, the space group, and the coordinates of the individual carbon atoms in the cell. The chains deviate slightly from the conventional planar zigzag structure, the vinyl group substituents are arranged in the 1–3 sequence, with alternating D and L configurations. It is proposed to call this type of spatial arrangement in head-to-tail vinyl polymers a syndiotactic arrangement. Also polyvinyl chloride, obtained with free radical catalysts, contains small ordered regions, with a structure similar to syndiotactic 1,2-polybutadiene.

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THE ENZYMIC SYNTHESIS OF RUBBER *

HOWARD J. TEAS

FIELD CROPS RESEARCH BRANCH, AGRICULTURAL RESEARCH SERVICE, UNITED STATES
DEPARTMENT OF AGRICULTURE, BELTSVILLE, MARYLAND

AND

ROBERT S. BANDURSKI

DEPARTMENT OF BOTANY AND PLANT PATHOLOGY, MICHIGAN STATE
UNIVERSITY, EAST LANSING, MICHIGAN

Studies of the mechanism of biosynthesis of rubber in seedlings and cultured tissues of guayule have established that the carbon of the isoprenoid chain can be derived exclusively from acetate¹, and flax enzyme preparations have indicated that the branched chain acids, β -methyl crotonic acid and β -methyl- β -hydroxyglutaric acid are probably intermediates in the formation of the basic isoprenoid unit². However, the requirement for intact plants or tissue cultures has made detailed studies of the biosynthesis of rubber difficult. We have now observed that incubation of C^{14} -labelled acetate results in the incorporation of radioactivity into rubber.

The time course of incorporation of sodium acetate into rubber is shown in Figure 1. Following incubation, the latex reaction mixture was coagulated by

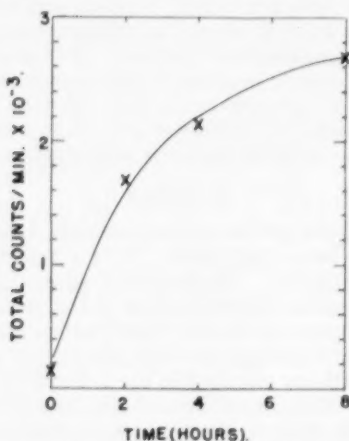


Fig. 1.—Time course of incorporation of 1- C^{14} -acetate into rubber: each incubation tube contained in micromoles, adenosine triphosphate 1, magnesium fructose diphosphate 2, CoEnzyme A 0.01, diphosphopyridine nucleotide 0.01, ethylenediamine tetraacetate 1, potassium phosphate 1, sucrose 60 sodium acetate 2 (containing approximately 5×10^4 c.p.m.), and latex 0.1 ml.; total volume 0.3 ml.; pH 7; incubation at 37° for the indicated time.

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acetone and the rubber was purified for counting by acetone and water extraction, solution in benzene-trichloroacetic acid, and precipitation as microcrystalline rubber bromide, $(C_8H_7Br_2)_n$. The addition of cofactors, as listed in the legend of Figure 1, stimulated the rate of incorporation of acetate into rubber approximately tenfold. Latex was also incubated with C^{14} -labelled sucrose, carbon dioxide, sodium β -methylcrotonate, and sodium pyruvate. It was found that sodium β -methylcrotonate and sodium pyruvate were incorporated at considerably lower rates than was sodium acetate and that sucrose and carbon dioxide were not incorporated.

The dependence of the incorporation of acetate into rubber on the concentration of latex in the incubation mixture is illustrated by the data in Table I.

TABLE I
EFFECT OF ENZYME (LATEX) CONCENTRATION OF ACETATE
INCORPORATION INTO RUBBER¹

Latex (cc.)	Radioactivity (counts/min./mg. carbon)
0.00	2.6
0.02	2.8
0.04	4.5
0.06	14
0.08	38
0.10	120
0.13	210

Latex was added to all tubes at the end of the incubation period and immediately inactivated by adding acetone so that equal amounts of rubber were present in all tubes for isolation and counting.

That the radiocarbon to acetate was, in fact, incorporated into rubber was demonstrated by degradation of a sample of the enzymically synthesized rubber to levulinic acid. The specific activities of rubber bromide isolated as in the above experiments, of rubber bromide isolated after preliminary purification of the rubber by alcohol, and of the 2,4-dinitrophenylhydrazone of levulinic acid prepared from the purified rubber were 220, 200, and 230 counts, respectively, per minute per milligram of rubber carbon.

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³ The reaction conditions were as for Figure 1 except for latex concentrations as indicated. The incubation time was 4 hours.

THE STRUCTURE AND VISCOSITY OF HEVEA LATEX. I.*

G. VERHAAR

FIRESTONE PLANTATIONS CO., LIBERIA

INTRODUCTION

In recent years the complex nature of Hevea latex has been the subject of a number of investigations in which it was established that besides the rubber particles another dispersed phase is present in the aqueous serum. These irregularly shaped, viscous, colloidal bodies were first described by Miss Homans and van Gils¹ and called lutoids because of the fact that when fresh undiluted latex is centrifuged these bodies are collected at the bottom of the tube and show a more or less yellow appearance. Investigations in this laboratory showed that the yellow color is not an intrinsic property of these bodies, the color of the yellow fraction being caused by the presence of carotenoids dissolved in the Frey-Wyssling globules and the name viscoids was proposed instead², since their high viscosity was considered to be truly characteristic.

When fresh Hevea latex is observed microscopically the viscoids appear as capriciously shaped, jelly-like bodies of greatly varying size, ranging from about 5 to more than 200 microns (greatest length). They do not possess rigid forms but change easily under slight pressure. Obviously in rheological experiments with Hevea latex the occurrence of the viscoids will greatly influence the results. Another factor involved is that freshly tapped latex changes within the course of 24 hours from a liquid into a solid coagulum (gel formation). In carrying out viscosity measurements it is therefore necessary to maintain a rigid time schedule in order to obtain comparable results. From an academic standpoint as well as with a view to the handling of latex in estate practice it would be of interest to determine the influence of the addition of common preservatives, such as ammonia, sodium sulphite, and formaldehyde, and the effect of dilution on the viscosity. In this paper special attention will be paid to a possible relationship between the various viscosity phenomena and the occurrence of viscoids.

GENERAL PROCEDURE

All viscosity measurements were carried out with a Brookfield synchroelectric viscometer, model LVF. The operating principle of this instrument is the measurement of the drag produced upon a spindle rotating at a definite constant speed while immersed in the material under test. A series of spindles of various capacities is provided, each covering, in centipoises, a specific range of viscosities. Provisions are also made to obtain changes of speed (6-12-30-60 r.p.m.). The drag is indicated on a rotating dial by a pointer and viscosities are found either by direct reading or by multiplication with a simple factor. The instrument is particularly useful for viscosity measurements in non-Newtonian liquids as it provides a means of determining the presence and extent of structural viscosity and other rheological properties.

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In working with fresh latex the following time schedule was maintained:

The latex to be investigated was collected from the cups on a given clonal plot between 8:00 and 9:00 a.m. This latex was brought to the laboratory and screened through a round-hole sieve, having perforations of 0.5 mm. diameter; it was then treated with various amounts of preservative or water between 9:45 and 10:15 a.m. Viscosity measurements were carried out from 10:15 to 11:45 a.m. at room temperature (28° to 29° C) and immediately afterwards all samples were observed through the microscope.

By this method the influence of the time factor was minimized as much as possible and comparable results were obtained. This does not necessarily mean that the data found are directly related to those determined with other instruments.

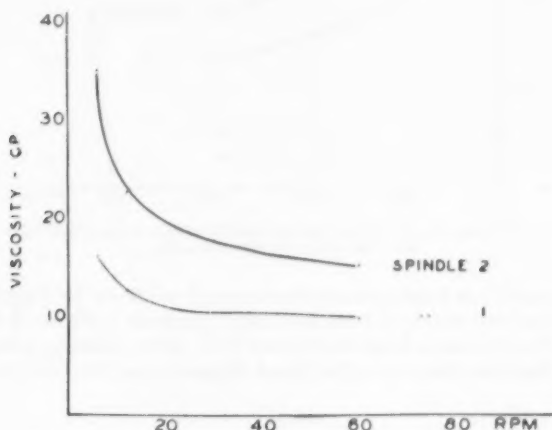


Fig. 1.—Influence of rate of shear on the viscosity of ammoniated latex.

The value used for calculation of the viscosity was the average of six readings, each reading taken after a rotation of the spindle of 30 seconds and a period of 10 seconds for stopping the dial and allowing the pointer to return to zero.

STRUCTURAL VISCOSITY OF HEVEA LATEX

To determine the influence of rate of shear on the viscosity of the material under test the spindle of the Brookfield viscometer was run at four different speeds (6–12–30–60 r.p.m.). The influence of friction between spindle and liquid could be ascertained by changing spindles (the cylindrical body on spindle No. 1 has the same diameter as on spindle No. 2 but a length of 65 mm. against 7 mm. for spindle No. 2), providing in both cases that readings do not exceed 100. For Hevea latex only spindles No. 1 and No. 2 can be used.

Figure 1 gives a typical example of the influence of friction and rate of shear on the viscosity of ammoniated field latex. It shows that the viscosity value greatly depends not only upon the rate of shear, but also upon the size of the spindle. An increasing speed yields a gradually decreasing viscosity value, whereas a larger friction surface gives a further decrease. The same phenom-

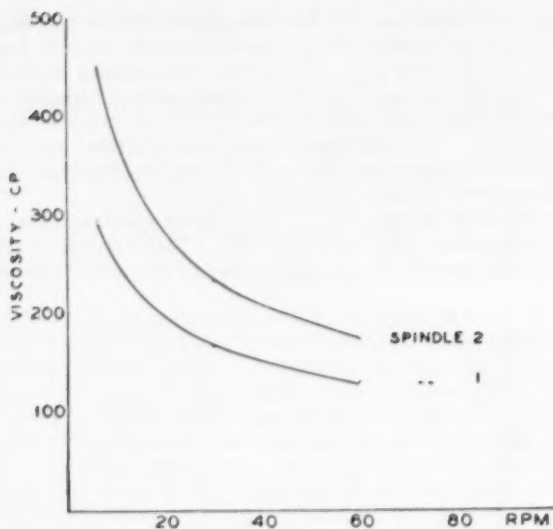


FIG. 2.—Influence of rate of shear on the viscosity of latex concentrated to 61% DRC and preserved with ammonia.

enon is observed when latex concentrate is tested as shown by Figure 2. Two examples of viscosity curves of fresh field latex are given in Figure 3, Curve A as typical for a high viscosity latex and Curve B for a low viscosity latex.

The fact that the viscosity value found depends upon the conditions during

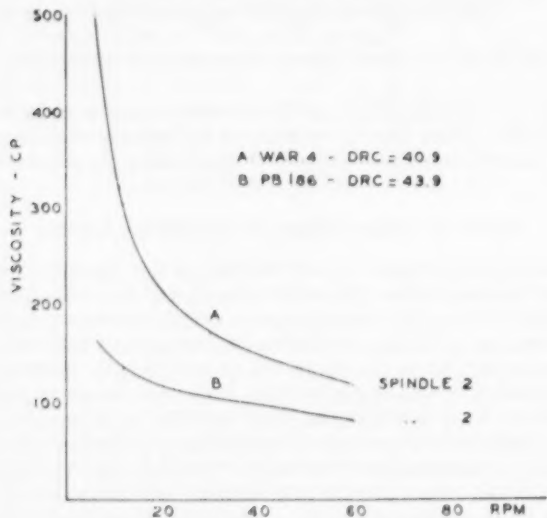


FIG. 3.—Influence of rate of shear on the viscosity of fresh field latex.

measurement is a characteristic of concentrated non-Newtonian liquids and it is clear from the curves given that Hevea latex, be it fresh, ammoniated, or concentrated, can be regarded as such.

The occurrence of structural viscosity is, in general, caused by two factors: first, the formation of a structure in the sol, and second, a hydrodynamic influence on the orientation of the dispersed particles in relation to their shape and size. Now in Hevea latex it can be assumed that one of the factors contributing to the colloidal stability is the orientation of a number of water molecules around each rubber particle in a water mantle with a structure that prevents free Brownian movement of these molecules. When the latex is at rest

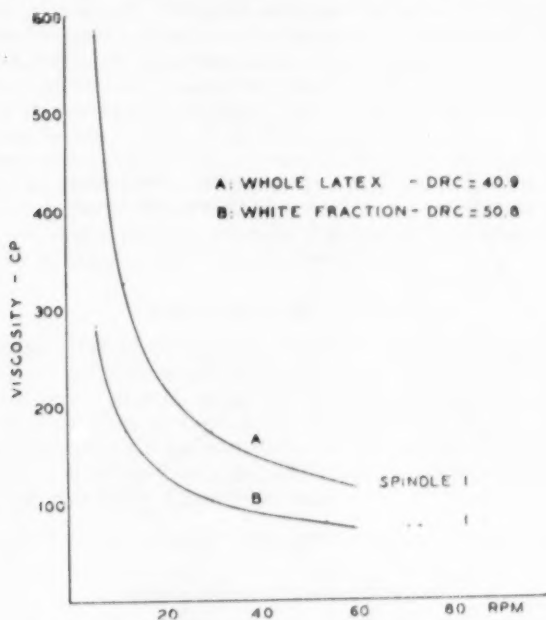


FIG. 4.—Influence of viscid removal on viscosity of fresh field latex.

an appreciable amount of water will be immobilized in this way, giving the system a very high intrinsic viscosity. However, when a force is applied to this system of a magnitude considerably in excess of the forces binding the water molecules, this will cause a rupture of the bond between water mantle and rubber particle, destroy the internal structure of the latex to a certain extent, and therefore lower the viscosity.

The second factor, orientation of the dispersed particles under hydrodynamic influence, will be less important for the rubber particles which are globular or slightly pear-shaped, but may greatly influence the results in fresh unpreserved Hevea latex, still containing the viscoids in their original shape and size. From the fact that they are up to a hundred times bigger than rubber particles and easily change their shape under slight pressure, it can be assumed that orientation around the rotating spindle is readily obtained. The presence

of viscoids in Hevea latex can therefore be considered as a contributing factor in causing structural viscosity.

Viscosity determinations on fifteen samples of fresh latex with different DRC's showed no correlation between DRC and viscosity. This does not, of course, mean that in fresh latex the number of rubber particles has no influence on viscosity, but that this factor is masked by other factors influencing the structure of fresh latex, *inter alia*, by the number, size, and rigidity of the viscoids present. The addition of ammonia causes a profound change in the size and shape of the viscoids² and relationships between DRC and viscosity which have been proposed for ammoniated latex³ can hardly be expected to apply to fresh latex.

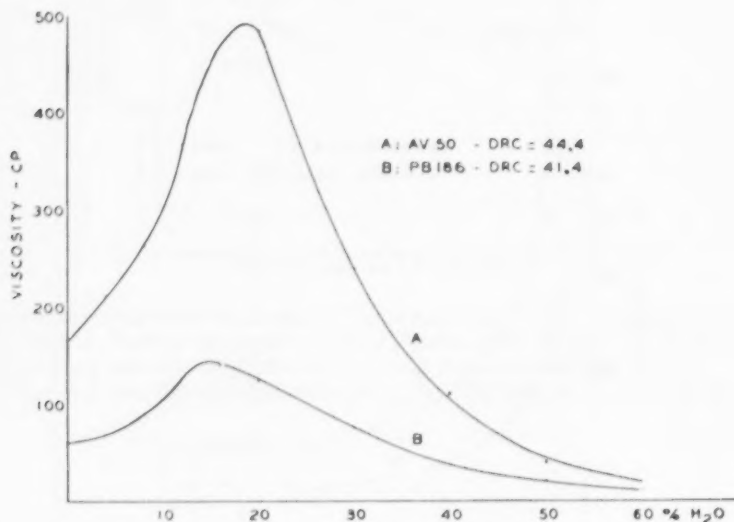


FIG. 5.—Viscosity of latex-water mixtures.

The influence of the viscoids on the viscosity can also be demonstrated by determining the viscosity of a fresh latex and of the white fraction prepared therefrom by centrifuging. An example is given in Figure 4, showing that the whole latex yields considerably higher values than the white fraction, although the original DRC was 40.9 against 50.8 per cent for the white fraction. Removal of viscoids by centrifuging thus results in a low viscosity latex with a higher DRC.

INFLUENCE OF DILUTION

It is well known in estate practice that rain dilution of field latex often causes trouble in handling the latex prior to coagulation due to a tendency to pre-coagulation in the field. Although not much is known regarding the causes it is usually ascribed to the effect of bark substances extracted by the rain⁴ and little attention had been paid to the effect of pure water. It was therefore considered

of interest to ascertain the effect of distilled water on fresh field latex regarding its viscosity and tendency to precoagulation.

In preliminary experiments it could be established that in some cases the addition of certain amounts of water caused a considerable increase of the viscosity; therefore spindle No. 2 at 30 r.p.m. was used in the measurements. Data on two of these experiments are shown in Figure 5. It appears that addition of water up to 15 to 20 per cent on total volume causes an increase of the viscosity followed by a gradual decrease at higher dilutions. It is interesting to note that latexes diluted with about 35 per cent of water had the same viscosity as the originals.

Following the process of dilution microscopically it could be observed that the increase in viscosity coincided with the formation of bigger viscid complexes, these complexes often including some of the rubber particles. This phenomenon showed a striking resemblance to the first stage of acid or spontaneous coagulation. It therefore seems that water alone in concentrations up to 20 per cent is able to cause a change in the physicochemical structure of latex which brings the latex into a stage of precoagulation.

The formation of bigger viscid complexes may be ascribed to two factors, clotting and swelling, the former caused by a decrease of the repulsive electrical forces and the latter by water transport from the serum into the viscoids as the result of a lowering of the ionic strength of the serum, assuming that serum and viscoids were in osmotic equilibrium before dilution.

INFLUENCE OF AMMONIA

As mentioned before, viscoids vary greatly in size and shape when observed in fresh latex; their greatest dimension may range from about 5 to 200 microns. When ammonia is added the structure of the latex is profoundly changed by complete disintegration of the viscid complexes into units, small globules, somewhat bigger than rubber particles². It was further found that increasing the ammonia content by very small increments brought about a rapid breakdown as illustrated in the following example:

TABLE I

Ammonia (per cent)	Average size of viscoids (microns)
0.000	30-200
0.025	15-100
0.050	5- 25
0.075	3- 15
0.100	3- 5
0.150	3- 5

When the viscosities of these latexes are determined, using a No. 1 spindle at 30 r.p.m., the results are as given in Figure 6. The curves show a fast drop in viscosity by addition of ammonia up to about 0.05 per cent, a break in the curve at that point, and a slightly decreasing viscosity at higher ammonia concentrations. The shape of these curves is in accordance with the results obtained by van Gils⁶.

It is known that the viscosities of fresh latex vary over a wide range and it is interesting to note that addition of ammonia evens out these differences. By comparing Table I and Figure 6 it can also be seen that in the region of 0.00 to 0.05 per cent, ammonia viscid disintegration and drop in viscosity coincide.

It is therefore tempting to assume, first, that the two phenomena are directly related and, second, that at ammonia concentrations below 0.10 per cent no relationship between DRC and viscosity is found because of the latex then being a heterogeneous mixture of viscoids and rubber particles. At higher ammonia concentrations such a relationship could be established¹ because latex under those conditions is a homogeneous mixture of viscoid units and rubber particles.

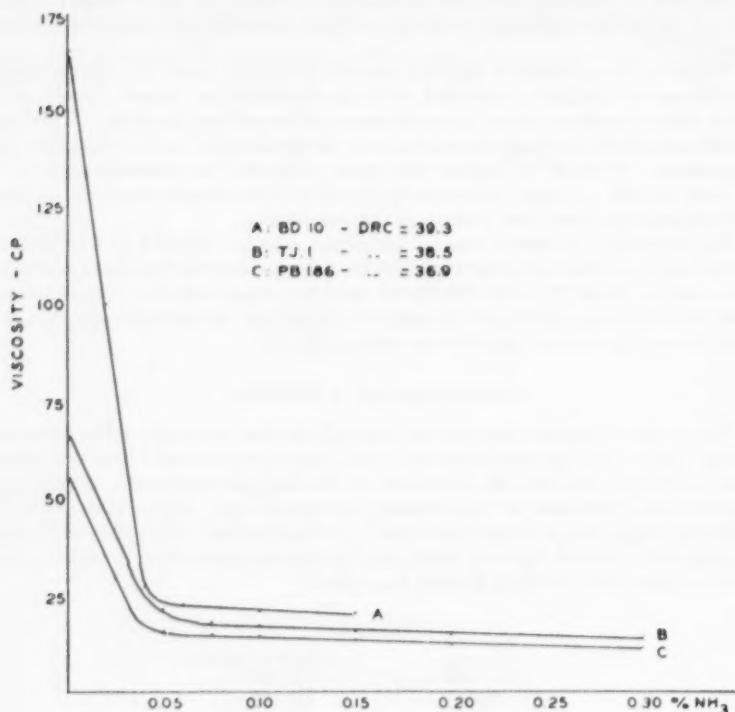


FIG. 6.—Influence of ammonia on the viscosity of fresh latex.

INFLUENCE OF SODIUM SULFITE

To ascertain the influence of sodium sulfite, still the most popular preservative for crepe production, on the viscosity of fresh field latex a series of experiments was set up along the same lines as described above. Samples of fresh clonal latex having no preservative were used and treated after screening with different amounts of a 10 per cent sodium sulfite solution up to 0.30 per cent. Viscosity measurements were carried out within the time schedule given and samples were studied microscopically immediately afterwards. The viscosity curves of two latexes thus treated are given in Figure 7; experiments with other clonal latexes showed similar results, i.e., addition of sulfite in increasing amounts causes a gradual decrease in viscosity with the curve sloping off and reaching a minimum at 0.25 to 0.30 per cent.

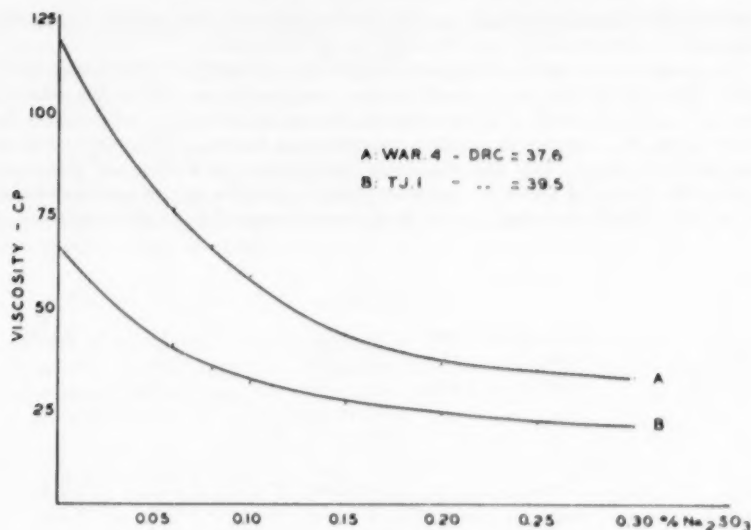


FIG. 7.—Influence of sodium sulfite on the viscosity of fresh latex.

Characteristic differences from ammoniated latex are, first, that the curves are smooth and do not show a break; second, that the minimum viscosity is reached at a higher level; and third, that in sulfited latexes no relationship could be found between DRC and viscosity.

Microscopic observations confirmed previous findings² that addition of sulfite to fresh latex tends to disintegrate the viscid complex partially. An estimate of the average particle size in such a latex would be approximately as in Table II.

On the basis of these observations the change of viscosity in sulfited latex can be assumed to be related to the behavior of the viscoids in that, first, the gradual disintegration runs parallel with a gradual decrease in viscosity and, second, the level of minimum viscosity is higher than in ammoniated latex because the average particle size of the viscoids is bigger. It can also be assumed that the presence of viscid complexes of varying sizes and shapes, not com-

TABLE II

Sulfite (per cent)	Average size of viscoids (microns)
0.00	70-150
0.02	50-100
0.04	30-70
0.06	25-50
0.08	20-50
0.10	10-50
0.15	10-30
0.20	5-30
0.25	5-30
0.30	5-30

pletely broken down into units at the minimum level of viscosity, masks the relationship between DRC and viscosity as in fresh latex.

The cause of the anticoagulating effect of sodium sulfite is still not entirely clear. The specific disinfecting action may play a role as well as the alkaline reaction⁶, but in the light of these experiments one is inclined to believe that the action upon the viscoids is another contributing factor. This may even be generalized by stating that any change in Hevea latex by addition of chemicals or otherwise bringing about a conglomeration of viscoids causes precoagulation and, on the other hand, any change that is accompanied by a disintegration of

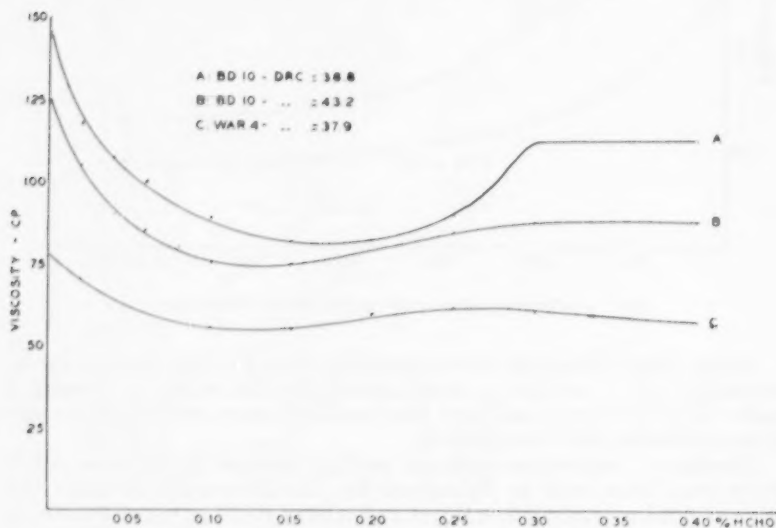


Fig. 8.—Influence of formaldehyde on the viscosity of fresh latex.

the viscoids tends to stabilize the latex. Microscopic investigation of the effect of added chemicals on the behavior of the viscoids could thus provide a new tool in the search for other and better preservatives.

INFLUENCE OF FORMALDEHYDE

The use of formaldehyde as a preservative in field latex is apparently still a controversial subject. While some object to its use⁷, others particularly favor it, as in the preparation of USF rubber⁸. Objections are on the ground that formaldehyde has a tendency to cause curdling or clotting in Hevea latex. As this would probably influence the viscosity, a number of formaldehyde treated latexes were tested, of which Figure 8 gives a few examples. As can be seen from these curves addition of formaldehyde up to about 0.15 per cent causes a slight decrease in viscosity followed by an increase to an end value for 0.40 per cent of about the same magnitude as the original latex. It should be mentioned here that some curves determined showed irregularities at low concentrations

of formaldehyde, although the over-all picture was the same as that given in Figure 8.

It had been found previously that the viscid volume, as determined by centrifuging, was increased somewhat by addition of formaldehyde and this was attributed to a possible increase in packing volume². As viscoids are known to be rich in protein⁹, a contributing factor in this could be the formation of condensation products of formaldehyde and proteins. Microscopic observations of the various samples did not reveal a clear, measurable change in particle size of the viscoids, in accordance with the relationship between viscoids and viscosity as discussed previously.

ABSTRACT

Fresh Hevea latex is characterized by the presence of viscoids of greatly varying size (5–200 microns). When the viscosity of such a latex is determined with a viscometer of the rotary type the values found cover a wide range, having no clear relation to the initial DRC of the latex. Also, with the aid of a rotary viscometer, the structural viscosity of fresh or any other type of latex can be clearly demonstrated. When fresh Hevea latex is treated with ammonia in increasing amounts there is a sharp and regular drop in viscosity up to 0.05 per cent NH_3 . This runs parallel with a gradual and finally complete disintegration of the viscoids. Treatment with sodium sulfite in increasing concentrations up to 0.30 per cent yields a more slowly decreasing viscosity with end values approximately twice as high as with ammonia. Microscopic investigation shows a slow and only partial breakdown of the viscoids in the same area. Formaldehyde gave irregular results, but, in general, did not decrease or increase the initial viscosity considerably, neither could any influence be established on the size and shape of the viscoids. The viscosity of fresh Hevea latex is profoundly influenced by addition of distilled water giving a considerable increase up to 20 per cent and a sharp drop afterwards. Latex diluted with 20 per cent of water was microscopically found to be in a stage of pre-coagulation, with the immobilized rubber particles embedded in the viscid complexes. It is concluded that the viscoids play a dominant role in viscosity phenomena of Hevea latex.

ACKNOWLEDGMENT

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THE STRUCTURE OF HEVEA LATEX AND ITS VISCOSITY. II*

G. VERHAAR

FIRESTONE PLANTATIONS CO., LIBERIA

INTRODUCTION

In a previous paper a method was described to ascertain the influence of added chemicals and of dilution on the viscosity and structure of Hevea latex¹. It was found that Hevea latex shows the structural viscosity typical for non-Newtonian liquids and that the viscosity value is profoundly influenced by either water, ammonia or sulfite. These viscosity phenomena were studied in relation to the occurrence of viscoids and viscoïd complexes and it was concluded that the viscoïds play a dominant role in viscosity phenomena in Hevea latex.

In continuation this paper deals with the effect of dilution on the viscosity of sulfite or formaldehyde treated and ammoniated latexes, the relationship between viscosity and DRC for ammoniated field latex and diluted concentrate and the influence of the tapping cycle on the viscosity of whole latex and white fraction latex.

VISCOSITY OF LATEX-WATER MIXTURES

Additional experiments confirmed previous findings that the addition of distilled water profoundly influences the viscosity of fresh field latex. It appeared that addition of water up to 15-20 per cent on total volume causes a considerable increase followed by a gradual decrease at higher dilutions. The increase in viscosity coincides with the formation of bigger viscoïd complexes, as occurs also in the first stage of acid or spontaneous coagulation. It therefore seems that water alone in concentrations up to 20 per cent is able to cause a change in the physico-chemical structure of fresh field latex which brings it into a stage of precoagulation.

For an explanation of these phenomena it may be considered that water in Hevea latex is present in three different forms: a) as the vehicle for the suspended rubber particles, viscoïds and Frey Wiesling globules, at the same time acting as solvent for salts and other non-rubber constituents that are in true solution; b) as a hydration shell around each individual rubber particle in which the water molecules are arranged in a semicrystalline structure, thereby hindered in their Brownian movement and thus contributing to the stability of the colloidal system; and c) as the main constituent² of the viscoïds (75-87 per cent), in which it may be separated from the "free" water by an enveloping membrane³.

In this system viscoïds and serum are supposedly in osmotic equilibrium. Now when fresh field latex is diluted the main immediate effect would be the disturbance of this osmotic equilibrium by a decrease in the ionic strength of the serum. Because of this the viscoïds start to swell by taking up more water from the diluted serum to restore the equilibrium. The formation of these bigger complexes offers a plausible explanation for the initial increase in viscosity of water diluted latex. This view is supported by the fact that latex can be diluted without any apparent change in the viscoïds using a 0.1 N solution of a

* An original publication.

salt² such as NaCl or KCl. In that case the osmotic equilibrium would be maintained.

On addition of increasing amounts of water there apparently comes a point where the complexes have reached their maximum size, coinciding with the peak in the viscosity curve. By addition of still more water the structure of the viscid complexes will be destroyed and the individual viscoids cease to exist because the enveloping membranes burst and the gelatinous central bodies (called "luteum" by Miss Ruinen², which in our terminology would be "viscum") are dispersed in the serum and mix homogeneously, although many constituents may still occur in a macromolecular (colloidal) state. This phenomenon is then accompanied by a steep drop in viscosity of the diluted latex.

Most clonal latexes have an initial Brookfield viscosity (1) No. 2 Spindle at 30 r.p.m. between 120 and 180 cp, and a maximum viscosity between 300 and 450 cp. This maximum is reached after dilution with an amount of water varying from 16 to 20 per cent on total volume. However, PB.186 latex seems to be an exception in that it has a lower initial viscosity (around 60 cp) and a much lower maximum viscosity on dilution (around 140 cp).

TABLE I

No. Sample	Latex, ml	Water, ml	Dilution, %
1	250	0	0
2	240	10	4
3	230	20	8
4	220	30	12
5	210	40	16
6	200	50	20
7	175	75	30
8	150	100	40
9	125	125	50
10	100	150	60

No relationship could be found between the maximum viscosity at dilution and the DRC, or between the percentage of water at the maximum and the DRC.

RELATION BETWEEN VISCOSITY AND DILUTION FOR SULFITED LATEX

The effect of sodium sulfite on the viscosity of fresh field latex has been described before¹. It was found that addition of sulfite in increasing amounts causes a gradual decrease in viscosity with the curve sloping off and reaching a minimum at 0.25–0.30 per cent sulfite. Since the addition of water to untreated latex shows an entirely different picture the effect of dilution was determined in latex that had been sulfited previously.

For this purpose clonal samples were collected, sulfited in the field with the proper amount of sulfite in a 10 per cent solution, screened and diluted with various amounts of water according to Table I. Viscosity measurements were carried out at room temperature (28–30° C). Some typical examples of the results obtained are given in Figure 1. It appears that at low sulfite concentrations (curve A) the shape of the dilution curve is very much like those obtained by dilution of unpreserved field latex.

However, at higher sulfite concentrations (curve B) the dilution curve shows some characteristic differences. After an initial decrease up to about 15 per cent dilution the viscosity rises again until a maximum is reached at 45 per

cent dilution. This maximum is not only shifted to a more diluted latex but is also much lower than in unpreserved latex. Further experiments showed that at still higher concentrations (curve C) the minimum occurs at about 30 per cent dilution and the maximum at about 50 per cent.

Now when these curves are considered in relation to the structure of Hevea latex an increase in viscosity means the formation of bigger viscid complexes as an introduction to coagulation. Therefore, the most effective preservative would be the one that not only disintegrates the viscid complexes and lowers the viscosity of undiluted latex but also yields a dilution curve that, at a reasonable concentration of preservative, does not show a maximum at any percentage of dilution. It follows that ascertaining the effect of a preservative on

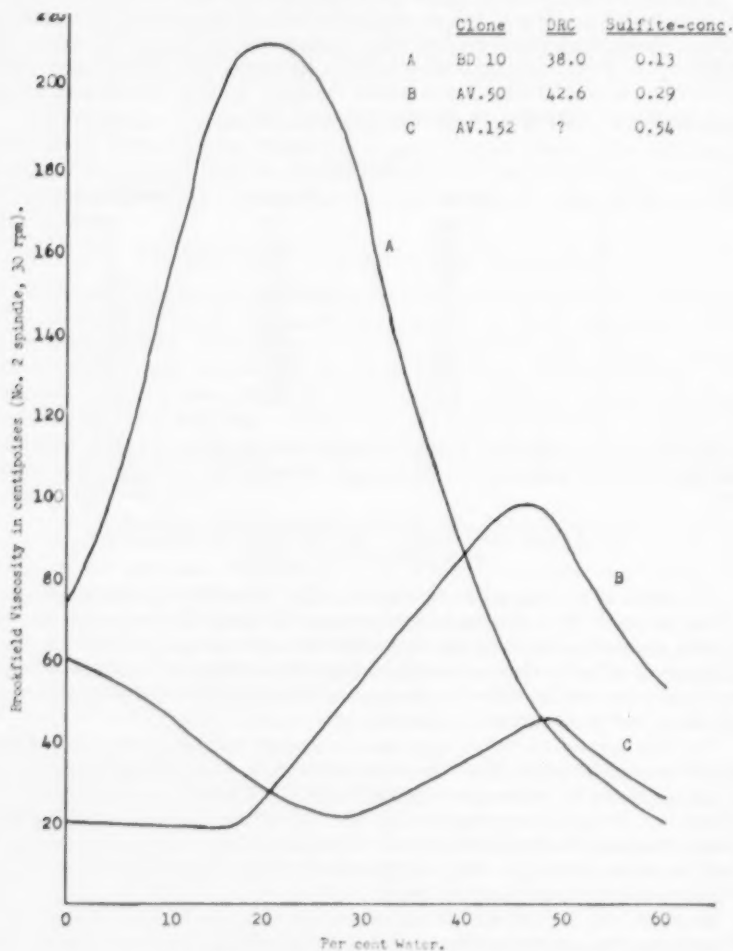


FIG. 1.—Viscosity of Sulfited Latexes on Dilution.

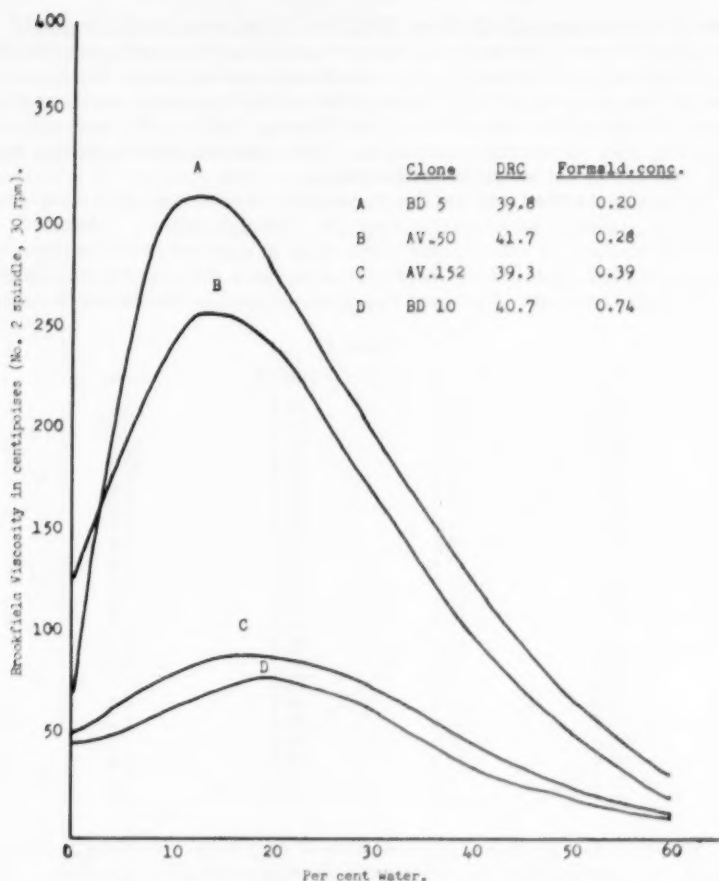


FIG. 2.—Viscosity of Formaldehyde Treated Latexes on Dilution.

the viscosity of undiluted field latex and the effect of dilution on the viscosity of preserved latex gives a new and easy method of evaluating the effectiveness of a preservative.

VISCOSITY OF FORMALDEHYDE TREATED LATEXES ON DILUTION

Addition of formaldehyde to fresh field latex does not decrease or increase the initial viscosity to any great extent, neither could any influence be established on the size and shape of the viscoids¹.

The effect of dilution on field latex treated with formaldehyde at various concentrations is shown in Figure 2. Curve A represents a BD 5 latex, DRC = 39.8 per cent, containing 0.20 per cent formaldehyde. This curve resembles those found for unpreserved latexes, except that the maximum viscosity occurs at a lower level (315 cp) and at a lower percentage of dilution (12 per cent).

Curve B represents an AV.50 latex, DRC = 41.7 per cent, containing 0.28 per cent formaldehyde. Here the maximum viscosity is 257 cp at 15 per cent dilution. Increasing the formaldehyde concentration yields curves like C and D. Curve C represents an AV.152 latex, DRC = 39.3 per cent, containing 0.39 percent formaldehyde; curve D is a BD 10 latex, DRC = 40.7 per cent, and containing 0.74 per cent formaldehyde. The latter one shows a slight maximum only (79 cp) at 20 per cent dilution.

The results obtained indicate that formaldehyde at a reasonable level of concentration is unable to counterbalance the "dilution effect". However, the maximum viscosity is considerably lower than in unpreserved latex, especially at higher formaldehyde concentrations, in accordance with its preserving action. According to the theory, developed in a previous section, this seems to indicate

TABLE II

DRC, %	Viscosity, cp	DRC, %	Viscosity, cp
42.0	16.8	34.2	9.0
41.8	17.0	34.0	9.75
40.2	14.4	34.0	11.4
39.6	15.0	33.8	10.0
38.2	11.8	33.7	10.0
38.1	14.5	33.5	7.95
37.9	14.6	33.4	9.4
37.9	15.5	33.1	10.4
37.2	12.8	32.7	8.5
37.0	11.3	32.6	10.0
36.9	11.6	32.5	7.4
36.2	9.2	32.2	9.5
36.2	10.1	31.9	10.3
36.1	10.3	31.7	10.25
35.9	7.8	31.7	10.7
35.9	10.2	30.1	7.4
35.7	13.0	29.9	8.4
35.5	12.4	29.9	7.2
35.4	12.8	28.7	6.8
34.9	9.8	27.9	7.0
34.7	10.5	27.8	6.6

that formaldehyde prevents the formation of very large viscid agglomerates, possibly by a partial fixation of the proteinaceous enveloping membrane. The maximum found also explains why dilution of formaldehyde treated latex has the tendency to cause curdling or clotting.

VISCOSITY OF AMMONIATED FIELD LATEX AND CONCENTRATE AND EFFECT OF DILUTION

Data on the viscosity of ammonia preserved and concentrated latex have been published by authors who tried to establish a satisfactory relationship between the DRC and the viscosity. Baechle⁵ reports agreement between results obtained on latex up to a DRC of 45 per cent and the formula of Guth for suspensions of spheres. Rhodes⁶ derived expressions from a large number of observations on field latexes and concentrates, which expressed the viscosity within the range of 0-68 per cent DRC. Since these results were obtained with other instruments (pipet viscometer or Hoppler viscometer) a number of latex samples was tested by means of the Brookfield viscometer, model LVF, using the No. 1 spindle at 30 r.p.m. All tests were carried out at room temperature (28-30° C).

Results are given in Table II and Figure 3. In general, a higher DRC corresponds with a higher viscosity, however, it is obvious from the data presented that individual samples vary greatly in their DRC-viscosity relationship, so much so that no significant mathematical expression for that relationship could be established. Variations up to 40 per cent occur for viscosities at the same DRC and up to 13 per cent for DRC's at the same viscosity. Maximum deviations from the average curve amount to 34 per cent for viscosities and 11 per

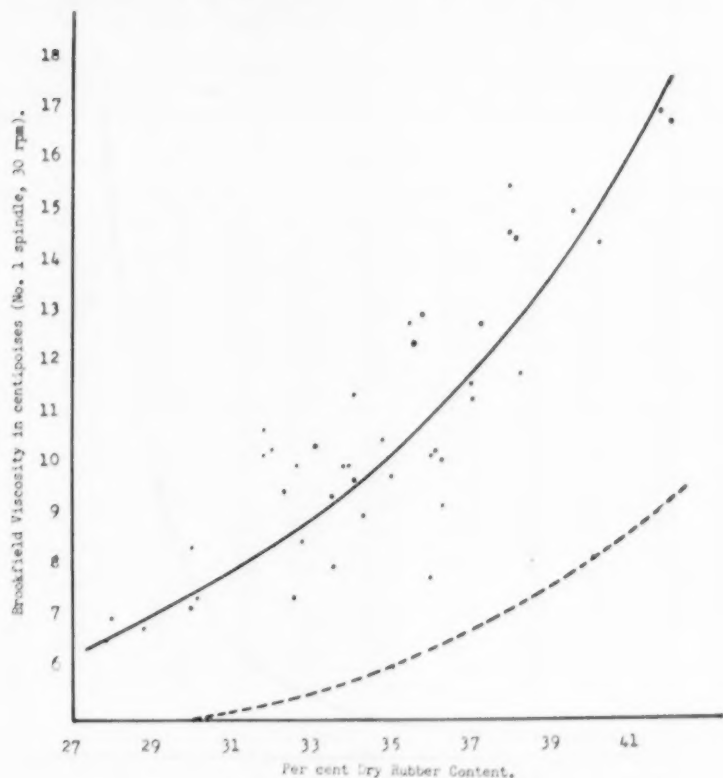


FIG. 3.—Viscosity-DRC Relationship for Ammoniated Field Latex.

cent for DRC. This also means that a viscosity determination cannot be used as a quick and easy method of establishing the DRC of ammoniated field latex. The lack of agreement between these results and previous findings is probably due to the fact that Baechle used diluted concentrate for his measurements and Rhodes based his expressions on a statistical method in which the results had been grouped into classes of 2 per cent DRC and the mean DRC and mean viscosity had been calculated for each class. The equations are claimed to give a reliable indication of the viscosity of "average" latex, but no mention is made of the accuracy for individual samples.

Besides the DRC there are apparently other factors that determine the viscosity of this kind of latex. Among these, variability in serum substances may play a role or differences in particle size distribution of the rubber particles, but in the author's opinion an important factor is the occurrence of the viscid units with their own structural variations in each individual latex. This view is supported by the fact that for concentrates a much closer viscosity-DRC relationship is found. This was established by determining the viscosity of a

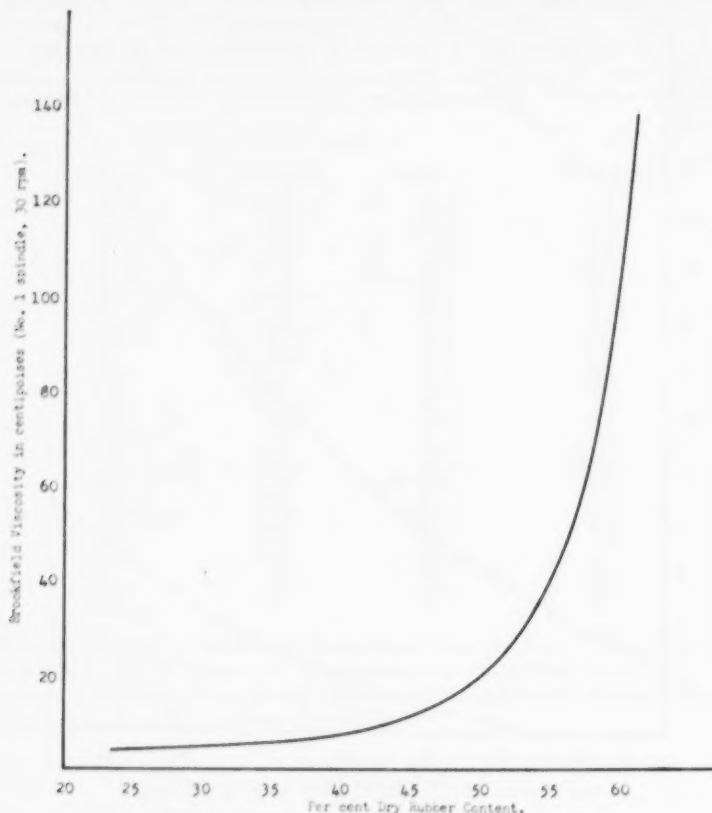


FIG. 4.—Viscosity-DRC Relationship for Diluted Concentrate.

number of concentrates, both as such and upon dilution with distilled water. The viscosity-DRC relationship for diluted concentrates is shown in Figure 4. All values found agree with the curve drawn within ± 5 per cent. This is still not accurate enough to permit the use of the viscosity value as a means of determining the DRC of a concentrate. However, it supports the view that the viscoids are being removed by centrifuging and is a demonstration of the effect of viscid removal on the uniformity of the resulting concentrate.

The shape of the curve in Figure 4 indicates that in this case addition of water does not cause any anomaly, in other words, the curve purely describes

the effect of dilution on the viscosity of a non-Newtonian liquid. The same type of curve is obtained when ammoniated field latex is diluted, however, the orders of magnitude of the viscosities of field latex and diluted concentrate are quite different. The dotted line in Figure 3 represents the portion of the concentrate curve in Figure 4 for DRC's from 30 to 42 per cent. It appears that at the same DRC the viscosity of diluted concentrate is considerably below that of field latex, due to the removal of viscoids during centrifuging.

INFLUENCE OF TAPPING CYCLE ON THE VISCOSITY OF WHOLE LATEX AND WHITE FRACTION LATEX

The study of the structure and viscosity of Hevea latex was continued with experiments aiming at establishing the influence of the tapping cycle on the viscosity of both unpreserved fresh latex and the white fraction prepared there-

TABLE III

Tapping day	Whole latex				White fraction			TS-DRC		
	TS, %	DRC, %	Visc.	Y.F., %	TS, %	DRC, %	Visc.	Latex	W.F.	DRC W.F.-L.
1	(47.5)	(44.7)	200	32.0	(53.3)	(50.6)	—	2.8	2.7	5.9
2	49.2	47.0	200	30.0	57.7	56.5	118	2.2	1.2	9.5
3	48.6	45.6	156	24.5	57.2	55.7	110	3.0	1.5	10.1
4	49.2	46.0	124	21.8	56.4	54.7	72	3.2	1.7	8.7
5	47.5	44.9	136	23.9	55.1	53.2	75	2.6	1.9	8.3
6	47.8	45.5	112	20.4	54.4	52.3	70	2.3	2.1	6.8
7	48.3	45.1	138	22.3	55.6	53.4	74	3.2	2.2	8.3
8	48.0	44.6	111	20.0	54.7	53.0	62	3.4	1.7	8.4
9	48.2	45.0	104	20.0	55.1	52.5	55	3.2	2.6	7.5
10	46.9	43.8	91	20.0	54.3	52.4	35	3.1	1.9	8.6
11	46.8	44.3	102	21.0	53.8	52.0	56	2.5	1.8	7.7
12	45.5	43.2	98	21.5	52.8	50.6	52	2.3	2.2	7.4
13	45.7	42.5	97	21.0	53.6	51.6	40	3.2	2.0	9.1
14	43.2	40.0	145	24.2	50.0	48.0	118	3.2	2.0	8.0
15	43.7	40.9	100	20.8	50.4	48.5	45	2.8	1.9	7.6
16	44.9	42.4	95	20.0	52.7	51.5	36	2.5	1.2	9.1
17	44.1	41.3	87	20.0	51.7	49.8	24	2.8	1.9	8.5
18	(26.1)	(24.0)	(59)	—	—	—	—	(2.1)	—	—
19	42.6	39.9	99	20.0	50.3	48.2	29	2.7	2.1	8.3
20	42.7	39.4	94	20.0	50.3	49.0	26	3.3	1.3	9.6
21	44.0	40.5	105	19.2	52.0	49.5	29	3.5	2.5	9.0
22	41.2	38.2	95	20.0	48.7	46.6	39	3.0	2.1	8.4
23	39.1	36.1	93	21.0	45.9	44.3	43	3.0	1.6	8.2

from, on the viscid volume and on the DRC and TS of both the whole latex and the white fraction. The latex (Tj.1) was collected from the same task each morning during a complete tapping cycle. The tapping system in use during the time was half spiral periodic, in periods of 23 days tap and 23 days rest (S/2, 23d/46, 100 per cent). The time schedule used to obtain comparable results was as follows:

Latex collected: 8:00-8:20; screened: 8:30; viscosity of fresh latex determined at 8:45; viscid volume determined by centrifuging: 8:45; separation of white fraction by centrifuging: 9:30; viscosity of white fraction determined at 10:00. The analytical data are given in Table III and presented in graphical form in the Figures 5, 6 and 7. They can be summarized as follows:

1. The DRC of the fresh latex gradually decreased from 47.2 per cent on the second day to 36.1 per cent on the 23rd day. It is a well recognized fact that in the course of a tapping cycle the DRC gradually falls off.

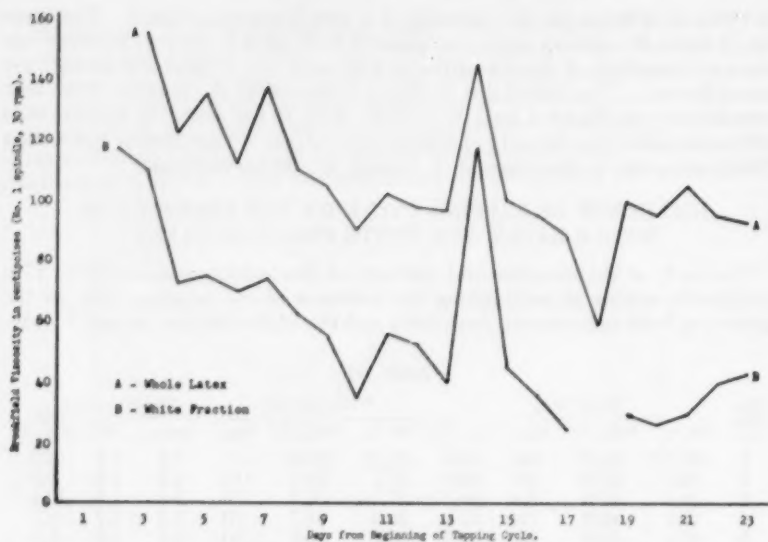


Fig. 5.—Influence of Tapping Cycle on the Viscosity of Unpreserved Field Latex and White Fraction.

2. The TS of the fresh latex decreased accordingly from 49.2 per cent to 39.1 per cent.

3. The maximum difference TS-DRC was 3.5 per cent and the minimum 2.2 per cent with an average of 2.9 per cent. The average DRC/TS value amounted to 93.7 per cent. No influence of the tapping day on the TS-DRC could be found.

4. The first two days the viscosity of the fresh latex was too high to measure as Brookfield viscosity 1/30. From the third to the ninth day the viscosity gradually decreased from 156 cp to about 100 cp and remained more or less constant for the rest of the tapping period. Exceptions were the fourteenth day

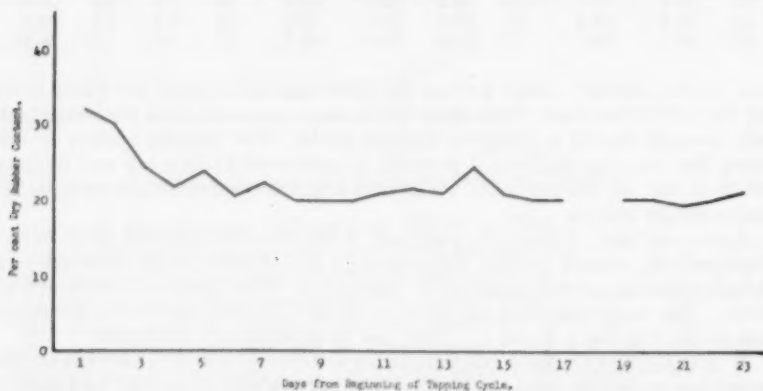


Fig. 6.—Influence of Tapping Cycle on the Viscid Volume of Unpreserved Field Latex.

on which the latex was affected by a slight rainfall and yielded a much higher viscosity and the eighteenth day with heavy rainfall which caused a very low viscosity. These results are in complete agreement with the influence of rain dilution as described before¹.

5. The viscid volume was highest on the first day (32 per cent) and decreased gradually till the eighth day to about 20 per cent, with exceptions on the two rainy days; the slight rainfall caused an increase to 24 per cent and the heavy rainfall reversed the order of white and yellow fraction in the centrifuge tube. Both phenomena were encountered before and explained on the basis of microscopic observations of water diluted latex⁶.

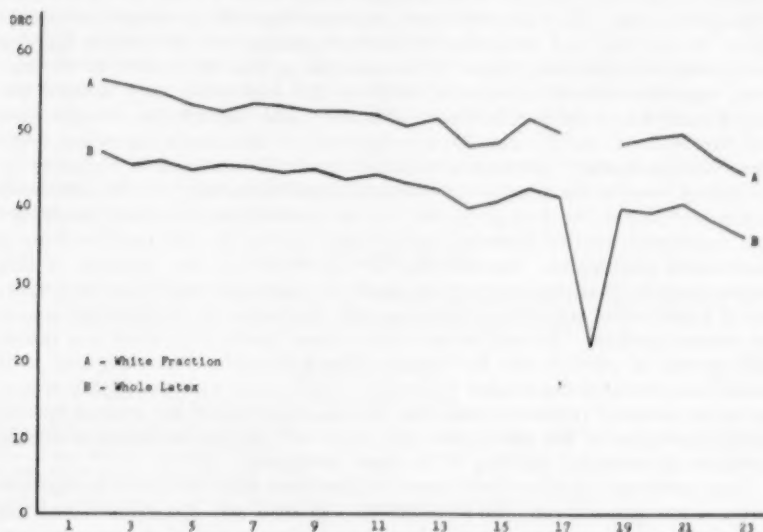


FIG. 7.—Influence of Tapping Cycle on the DRC of Unpreserved Field Latex and White Fraction.

6. The DRC of the white fraction was always considerably higher than that of the whole latex, the maximum difference being 10.1 per cent and the minimum 5.9 per cent with an average of 8.3 per cent, similar to an absolute increase of 19 per cent.

7. The maximum TS of the white fraction was 57.7 per cent and the minimum 45.9 per cent with an average of 53.0 per cent, similar to an absolute increase of 16 per cent.

8. The average difference TS-DRC for the white fraction was 1.9 per cent as compared to 2.9 per cent for whole latex. The average DRC/TS value for white fraction latex therefore amounted to 96.4 per cent as compared to 93.7 per cent for whole latex. These percentages give an indication of the purification that can be obtained by removal of viscoids by centrifuging.

9. Notwithstanding the higher DRC the viscosity of white fraction latex was much lower than of whole latex, the maximum being 118 cp and the minimum 24 cp. This is also attributable to the removal of viscoids. The difference in viscosity value of whole latex and white fraction varied from 46 to 76 cp.

10. The decrease in both viscosity and viscid volume of fresh latex run parallel up to the eighth day and both remain more or less constant for the rest of the period. On the other hand, the DRC falls off during the whole period. This is additional proof for the close relation between viscoids and viscosity in field latex.

POSSIBLE ROLE OF VISCOIDS IN LATEX FORMATION

In the preceding section the close relationship between viscoids and viscosity in field latex was mentioned. However, if the occurrence of viscoids was the only reason for the lack of agreement between viscosity and DRC in fresh latex, it could be expected that the white fraction would show a relationship between these two factors. This is not the case, whereas Figure 5 shows that the viscosities of whole latex and white fraction do run parallel over the entire tapping cycle, except the last two days. This could mean that the nature of the material, used by the rubber tree to build up the adsorption shell around the rubber particles, is another influencing factor. This leads to the thought that both this material and the viscoids are essentially of the same composition (proteins, phospholipids). From this point of view, this material is produced by the rubber tree for the purpose of creating colloidal stability for the dispersed rubber particles in the first place; the viscoids present as a separate phase, are then considered surplus material and nonessential in the end product from a biochemical standpoint. Speculating on the reason for the presence of this surplus material it is obvious that the amount of material needed for the formation of a protective adsorption shell is greatly dependent on the ultimate size of the rubber particle. Recent investigations have shown that there is a rather wide spread in particle size for various *Hevea* clones⁷. Now it seems as if nature has provided the rubber tree with a biochemical system capable of producing an excess of protective material, so that, regardless of the amount needed for the formation of the adsorption shell, there will always be enough available to ensure the colloidal stability of the latex produced.

In a recent article Schweizer⁸ gave as his opinion that the viscoids originate partly if not wholly from the sieve tubes. In that case the viscid material can only be considered as a "foreign body" or contamination of the latex proper. However, experimental work by Miss Ruinen and Mrs. De Haan-Homans⁹ has refuted this hypothesis. By anatomical examination it was found that in normal tapping not more than maximally 10 per cent of the functioning sieve tubes are cut and that latices, collected separately at various depths show the normal microscopic image with regard to the viscoids and a content of 20 to 30 per cent when centrifuged. Collected evidence from these and other findings therefore led to the conclusion that the viscoids do not enter the latex as a product of the sieve tubes, but only occur in the latex vessels². The parts of the plant tissue from which viscoids and rubber particles actually originate are still not known, but the possible role of viscoids in latex formation as discussed is not contrary to the occurrence of these bodies in the latex vessels according to the most recent investigations.

SUMMARY

This paper deals with the effect of dilution on the viscosity of sulfite or formaldehyde treated and ammoniated latexes, the relationship between viscosity and DRC for ammoniated field latex and concentrate and the influence of the tapping cycle on the viscosity of whole latex and white fraction latex. An

explanation is given of the shape of the viscosity curve of water diluted fresh field latex. It is shown that sulfite in increasing concentrations shifts the maximum viscosity of dilution to regions of higher dilutions and at the same time lowers the viscosity value at the maximum. In formaldehyde treated latexes the maximum viscosity in the dilution curve still occurs at 15-20 per cent dilution, but the maximum viscosity value is considerably lower, especially at higher formaldehyde concentrations.

Dilution of ammoniated field latex or concentrate yields a viscosity curve typical for a non-Newtonian liquid. The viscosity-DRC relationship for ammoniated field latexes shows wide discrepancies for individual samples and can not be used as a means for determining the DRC. Individual concentrate samples are in much closer agreement. The influence of the occurrence and removal of viscoids on these phenomena is discussed.

A description is given of the influence of the tapping cycle on the viscosity of unpreserved fresh latex and the white fraction prepared therefrom, on the viscid volume and on the DRC and TS of both whole latex and the white fraction.

Finally, the possible role of viscoids in latex formation is discussed in connection with some recent investigations concerning their occurrence in sieve tubes and latex vessels in the *Hevea* tree.

ACKNOWLEDGMENT

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POSSIBLE METHODS OF RECHARGING THE SURFACES OF PARTICLES OF LATEXES STABILIZED WITH SOAPS *

S. S. VOYUTSKIĬ, R. M. PANICH, AND K. A. KALYANOVA

Until the present time it was thought that the only latex particles capable of recharging their own surfaces were those of natural-rubber latex, stabilized with natural proteins the molecules of which contain two functional groups: the amino group, which causes the globules to have a positive charge in an acid medium, and the carboxyl group, which gives them a negative charge in an alkaline medium. In the case of synthetic latexes stabilized with soaps, it was supposed that in an acid medium the soap ceased to be a protective substance and that the latex must inevitably coagulate. Thus Maron and his coworkers¹, who used latexes stabilized with soaps in a study of the relation between the zeta-potential (electrokinetic potential) of the latex globules and the pH of the latex, were unable to lower the pH of the latexes below 5.5 because of the onset of coagulation.

Our previous work has shown, however, that in an acid medium under certain conditions it is possible for an emulsion to be recharged even though it be stabilized with substances which are incapable of changing the sign of the charge when the reaction medium changes. Such observations impelled us to make a more detailed study of the recharging of negatively charged particles in such emulsions with the aid of hydrogen and aluminum ions. The latex used in this work was a synthetic latex stabilized with ammonium oleate, with total solids of 28 per cent. The electrolytes used for the purpose of recharging the particles were hydrochloric acid and aluminum chloride, since the chloride ion has a comparatively small adsorptive capacity.

EXPERIMENTAL PART

RECHARGING THE GLOBULES OF THE LATEX BY THE ADDITION OF ACID

Even the first experiments showed that rapid addition of the acid and the proper latex concentration are necessary conditions for recharging the latex globules. Thus, the addition of decinormal hydrochloric acid to a concentrated latex invariably causes instant and complete coagulation. However, when hydrochloric acid is introduced into a latex solution containing only 2-4 per cent total solids, the coagulation either is only partially complete or does not occur at all.

In order to establish the relation between the zeta-potential of a latex and the pH of the latex solution after the addition of acid, we made use of a method which has often been used before². Borate buffer solutions were used as reference solutions; the pH and conductance values of the reference solutions were

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from the *Trudy Moskovskogo Instituta Tonkol Khimicheskoi Tekhnologii im. M. V. Lomonosova*, No. 4, pages 30-36 (1953). The present address of S. S. Voyutskii is the Lomonosov Institute of Fine Chemical Technology, Moscow, U.S.S.R.

TABLE I

pH	λ_0 (mhos)	Mean ζ -potential (millivolts)
10.8	5.86×10^{-4}	-57.0
8.1	7.36×10^{-4}	-82.0
6.5	1.05×10^{-3}	-64.4
5.2	1.21×10^{-3}	-29.4
3.5-4.5	—	The potential could not be measured because of coagulation
2.5	2.32×10^{-3}	+15.0
2.2	3.13×10^{-3}	+58.0
1.9	5.34×10^{-3}	+35.8
1.4	2.02×10^{-3}	+12.7

made equal to those of the liquids tested with the aid of hydrochloric acid and sodium hydroxide.

Each of the separate experiments was carried out in the following manner. 70 ml. of a hydrochloric acid solution of varying concentration was quickly added, with agitation, to an equal volume of a latex solution containing 4 per cent total solids. Then the specific conductance λ_0 and the pH of the solutions thus prepared were determined, after which reference solutions were prepared and the zeta-potentials were determined. The results of the determinations are presented in Table I and expressed graphically in Figure 1.

It is seen that, as the pH is lowered, the zeta-potential first rises markedly and then falls. This is followed by a region in which it is impossible to determine the zeta-potential because of the general loss of stability in the latex (the broken section of the curve). Beyond this region, with the addition of larger quantities of acid to the latex, the particles acquire a positive zeta-potential which rises sharply at first and then drops as still larger portions of acid are added.

Since the negative charge of the latex particles changes to a positive one when the latex is acidified, it follows that the latex must possess an isoelectric point. It proved impossible to locate this point by the method of electrophoresis, because the coagulation of the latex interfered; for this reason we found the point by means of determining the pH value corresponding to the maximum coagulation. It was found that the isoelectric point for the latexes used in this work was about pH 3.9.

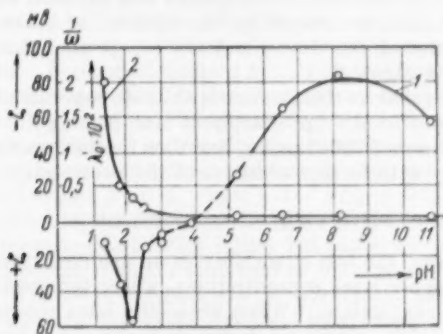


Fig. 1.—Influence of the pH value of the latex on its zeta-potential and specific conductance. 1, Zeta-potential. 2, Specific conductance. The abscissa represents the pH; in the ordinate the left-hand scale represents the zeta-potential in millivolts; the scale at right the conductance λ_0 in mhos $\times 10^3$.

RECHARGING OF THE LATEX GLOBULES BY THE ADDITION OF ALUMINUM CHLORIDE

Previous experiments have shown that the addition of aluminum chloride to a latex containing 2-4 per cent solids likewise causes only a partial coagulation and brings about a recharging of the globules remaining in the latex. We may note that the recharging in this case is achieved only when an equal volume of an aluminum chloride solution with a concentration of 0.001 *M* or above is added to the latex. Solutions of lower concentrations do not bring about such a recharge.

The addition of calcium chloride solutions of various concentrations to the latex, under any conditions whatever, invariably results in complete coagulation. However, when saturated potassium chloride solution is introduced into the latex, there is no coagulation but, instead, reversible flocculation.

In order to establish the relation between the zeta-potential of the latex globules and the amount of aluminum chloride added, we used the same method as in the previous set of experiments. A latex containing 4 per cent total solids was mixed with an equal volume of aluminum chloride solutions of various concentrations; the solution obtained was subjected to electrophoresis

TABLE II

Aluminum chloride concentration in the latex (moles)	pH	λ_0 (mhos)	Mean ζ -potential (millivolts)
0.02800	3.6	1.24×10^{-2}	+55.6
0.00280	3.8	1.62×10^{-2}	+65.6
0.00222	4.1	1.32×10^{-2}	+61.8
0.00111	4.1	7.72×10^{-3}	+55.6
0.00083	4.2	5.91×10^{-3}	+45.8
0.00055	7.2	5.40×10^{-4}	Rate of electro- phoresis = 0
0.00041	8.3	4.46×10^{-4}	-27.1
0.00027	8.9	4.77×10^{-4}	-47.3
0.0	9.8	3.94×10^{-4}	-82.0

at the same pH value which it had after the addition of the electrolyte. The reference solutions were aluminum chloride solutions in concentrations equal to the aluminum chloride concentrations of the mixed test solutions. The specific conductance of the reference solutions was adjusted with the aid of a sodium chloride solution, and its pH by the addition of borax or sodium hydroxide. The results of the determinations are presented in Table II and shown graphically in Figure 2.

The figure shows that as the aluminum chloride concentration in the latex increases, the zeta-potential drops sharply at first, passing through zero where the aluminum chloride is 0.00055 molar, and then reaches positive values which change only slightly with further additions of the electrolyte.

DISCUSSION OF RESULTS

As we have shown, the loss of stability in an acidified latex is a condition observed only in higher latex concentrations, where the conditions are especially favorable for coagulation. When we acidify latex solutions low in total solids content, in which collisions between particles occur fairly seldom, the system does not coagulate. The reason for this behavior is apparently that the latex remains stable in an acid medium as a result of the adsorption of positively

charged hydrogen ions by the globules. It is known that a hydrogen ion has a high adsorption capacity, and that in many cases it acts as a stabilizer. The literature makes mention of the possibility of recharging the particles of various colloids and emulsions with the aid of hydrogen ions, and in particular rubber globules originally stabilized with hydroxyl ions³.

The shape of the curve characterizing the relation between the change of the zeta-potential of latex particles and the change of pH in the latex can be explained easily. It is seen in Figure 1 that as the pH rises, the positive zeta-potential also rises at first. This is natural, since an excessively high acid concentration would tend to lower the zeta-potential and compress the double layer of ions on the particle. Such a phenomenon has been observed earlier in dilute emulsions of mineral oil. The positive zeta-potential reaches a maximum at pH 2 and then starts to drop because of a decrease of the hydrogen-ion concentration and an increase of the hydroxyl-ion concentration. At pH 3.9

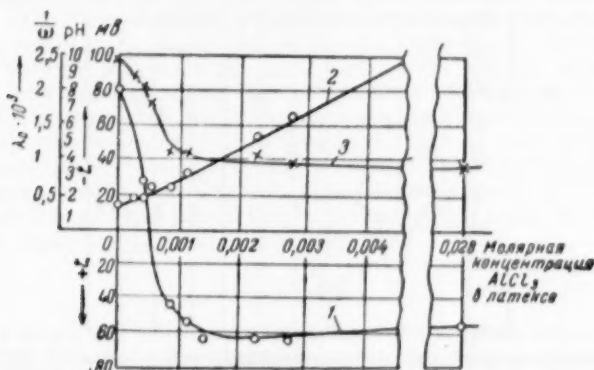


Fig. 2.—Influence of the aluminum chloride concentration in the latex on the zeta-potential, specific conductance, and pH value of the latex. 1. Zeta-potential. 2. Specific conductance. 3. pH. The abscissa represents the aluminum chloride concentration in moles of the mixed latex; in the ordinate the left-hand scale represents the conductance λ_0 in mhos $\times 10^3$, the middle scale the pH, and the scale at right the zeta-potential in millivolts.

the zeta-potential reaches zero; then, having acquired an opposite sign, the zeta-potential rises steadily as the pH increases, reaching a maximum at pH 8–9. This is because the soap content of the system increases as the fatty acid content decreases. It is logical that the weakly ionized fatty acid should stabilize the globules more poorly than the strongly ionized soap does. Maron's explanation¹ of the weaker stabilizing action of the acid, as being due to the poorer adsorption of the acid by the globules, is unsatisfactory in our opinion. The fatty acid, being the less soluble compound, is always adsorbed better by the rubber particles than soap is. It is a well-known fact that when latex is acidified, its surface tension is reduced. This is not caused by particles of fatty acid from the soap going into solution, but rather by the fact that the surface activity of the acid is higher than that of the soap.

After a pH of 9–10 is reached, the zeta-potential of the globules starts to drop again, since an excess of hydroxyl ions causes compression of the double charged layer just as an excess of hydrogen ions does.

The absolute values of the positive zeta-potential in an acidic medium are considerably lower than those of the negative potential in an alkaline medium.

This indicates that the recharged latex is less stable than the original latex, and that in this case the stabilizer present in the system is less active. The nature of the stabilizer is apparently also responsible for the fact that the curve of the zeta-potential slopes more gently to the right of the isoelectric point than to the left of it.

Let us now consider the effects noted when aluminum chloride is added to a sufficiently dilute solution. The situation in this case is complicated by two additional factors:

(1) When the latex is treated with aluminum chloride, the latter hydrolyzes partially or wholly, depending on the pH, with the result that the system acquires an acid reaction. Thus, when aluminum chloride is added to latex, the zeta-potential of the globules is influenced not only by the aluminum ions but also by the change of pH in the solution which is caused by the hydrolysis.

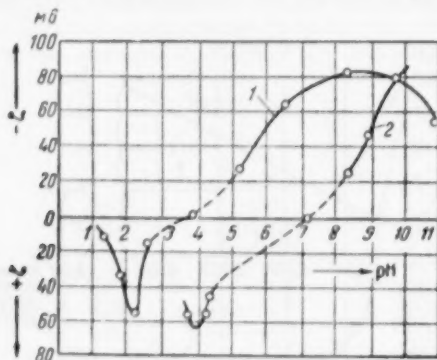


Fig. 3.—Relation between change of electrokinetic potential and pH of the latex. 1. With the addition of hydrochloric acid. 2. With the addition of aluminum chloride. The abscissa represents the pH, the ordinate the zeta-potential in millivolts.

(2) At pH 4 and above, insoluble amphoteric aluminum hydroxide is formed in the system, which is adsorbed by the rubber globules. One proof that the aluminum hydroxide is adsorbed by the particles of the dispersion, in our opinion, is the fact that the coagulum obtained under these conditions is entirely unlike that formed when the latex is acidified; it takes the form of a fine precipitate or porous lumps which can easily be crushed between the fingers. A coagulum of this type evidently results from the formation of a layer of aluminum hydroxide around the globules, which shields the rubber particles from direct contact with one another and thereby prevents the formation of the usual compact coagulum.

In order to exclude the effect of the pH value and to evaluate the action of aluminum chloride alone in the experiments where the latter was added to the latex, we may consider Figure 3. This diagram shows the change of the zeta-potential in relation to the pH in two sets of experiments. In one, varying amounts of aluminum chloride were added to the latex (Curve 2); in the other varying amounts of hydrochloric acid (Curve 1).

A comparison of the two curves shows that the introduction of aluminum chloride causes a marked shift to the right in a curve of the zeta-potential of particles versus the pH of the dispersion. However, both curves have the same shape.

Let us consider which ions can affect the charge of the latex particles when aluminum chloride is introduced into the system. The positive potential in this case can be governed by aluminum ions only at pH 4-4.1 or lower. At a higher pH, an amphoteric aluminum hydroxide is formed, which is adsorbed by the globules; the positive charge on the particles may be explained by the fact that their surfaces contain either $\text{Al}(\text{OH})_2^+$ or $\text{Al}(\text{OH})^{++}$ ions, or else by the presence of hydrogen ions, which are still found in the system and are also capable of being adsorbed.

The isoelectric point of aluminum hydroxide, as given in the literature⁴, is in the region of pH 7.5-8.0. This is confirmed by Curve 2, which intersects the abscissa at approximately this pH value. Evidently the electrical properties of the latex particles in this pH region are governed almost entirely by the layer of aluminum hydroxide adsorbed by the surface of the globules.

At still higher pH values, the aluminum hydroxide adsorbed by the globules becomes negatively charged, and $\text{Al}(\text{OH})_2\text{O}^-$ ions appear on the surfaces of the globules. It would seem that this would enable the negative zeta-potential of the globules to increase, in an alkaline medium, without any change of pH. Actually, however, this is not the case. Instead, the high pH values correspond to fairly small aluminum chloride additions. No increase is noted in the negative zeta-potential, which is governed by the hydroxyl ions, as a result of the added adsorption of $\text{Al}(\text{OH})_2\text{O}^-$ ions by the surfaces of the particles.

The aluminate, according to Daniels⁴, is usually formed at pH 6.8, but in the present work it could not be obtained. The latex with which we worked contained ammonia, and it is known that in the presence of ammonia, MAlO_2 is completely transformed into aluminum hydroxide.

CONCLUSIONS

1. It is shown that the surfaces of particles of a synthetic latex stabilized with soap can be recharged by acidification or by the addition of an aluminum salt.

2. It is established that a necessary condition for this recharging is a low-solids concentration in the latex, which makes it possible for the particles to be recharged without the formation of any considerable amount of coagulum.

3. The opinion is expressed that recharging by acidification occurs through the adsorption of positively charged hydrogen ions by the particles of the latex; recharging by the addition of aluminum salts is due to the formation of an amphoteric aluminum hydroxide which is adsorbed by the surfaces of the particles.

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EFFECT OF STORAGE CONDITIONS ON THE PROPERTIES OF LATEX. I.*

H. M. COLLIER

DUNLOP MALAYAN ESTATES, LTD., MALACCA

INTRODUCTION

The importance of oxygen absorption in affecting the properties of ammonia-preserved natural-rubber latex concentrate was first discussed in the literature in 1951. McGavaack and Bevilacqua¹ on the one hand and the Rubber Research Institute of Malaya² on the other showed that access of oxygen led to a marked increase of stability. Kidder³, however, who studied changes in properties over a period of a year, used a single sample of each latex under test and did not apparently take into account the increasing proportion of the latex exposed to air. He found that the mechanical stability time (M.S.T.) increased rapidly during the first month after tapping and concentration, reaching a maximum after 140 days and thereafter declining slowly. Other workers have confirmed his results in principle, and this plot of the change of M.S.T. with time has been generally accepted.

With the increasing use of the M.S.T. test as a measure of the quality of a latex concentrate, a number of interested groups have organized round-robin tests between the producer and consumer countries to ensure that M.S.T. results obtained with different instruments in different countries were truly comparable. Samples of a single latex concentrate, already at least a month old, have been despatched from Malaya and tested in a number of different countries on the same date. Lack of agreement has been frequent and the differences recorded have been much greater than those ascribable to instrumental differences.

Very recently, van den Tempel, Kraay, and Lunshof⁴ have published further results on the effect of seasonal variations on latex properties. They referred again to the marked effect of oxygen on mechanical stability. Although in the progress of their work samples of latex taken from a ship's tank in Sumatra were flown to Holland, testing was delayed until after the ship's arrival. It was, therefore, impossible to judge how the mechanical stability of the latex altered during shipment. Actual changes of mechanical stability during shipment are the starting point of the investigation recorded below.

RESULTS AND DISCUSSION

Ammonia-preserved centrifuged latex concentrate, with which this paper is concerned, is normally shipped from Malaya when it is about two months old. Based on Kidder's results, a slight increase of M.S.T. might be expected during transshipment. When, however, the M.S.T. of a sample taken from a ship's tank in Singapore is compared with that of one taken from the same tank on arrival in the U.K., the U.K. figure is almost always the lower of the two

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(samples always being taken in full bottles and tested within one week). In figures obtained over the last six months, this fall has averaged more than 15 per cent.

To try to discover the reason for this marked fall during shipment, a large sample of latex was taken from a certain ship's tank before it left Singapore. The M.S.T. was immediately determined and the sample divided in three, one sample being sent to the U.K. by air in a full bottle (Sample 1) and the other two being kept in Malaya, one in a full winchester bottle (Sample 2) and the other in a partially-full winchester (Sample 3). A fourth sample (Sample 4) taken at Singapore and sealed into a full winchester travelled to the U.K. on board the latex tanker, while a fifth (Sample 5) was taken from the ship's tank

TABLE I
MECHANICAL STABILITY RECORDED ON SAMPLES TAKEN FROM A SINGLE
SHIP'S TANKS OF CENTRIFUGED CONCENTRATE

Sample No.	Description of sample	Day tested	Full (F) or standing in presence of air (A)	M.S.T. tested in	
				Malaya	U.K.
—	M.S.T. of latex at time of shipment from Singapore	—	—	1089"	—
1	Sample sent by air to U.K. in a full bottle	19th	F	—	995"
	Retested in U.K.	32nd	F	—	910"
2	Returned by air to Malaya in a full bottle	62nd	F	778"	—
	Sample kept for 3 weeks in a full bottle in Malaya	21st	F	982"	—
	Sample continued to stand in the same bottle which had an appreciable air-space above the latex				
	Retested	28th	A	1386"	—
3	Sample kept for three weeks in a partially-full bottle in Malaya	51st	A	1514"	—
	Retested	21st	A	1180"	—
4	Sample taken at Singapore kept in a full bottle and carried to U.K. on board the latex tanker	54th	A	1860"	—
	Retested in U.K.	28th	F	—	830"
	Retested in U.K.	62nd	F	—	795"
	Returned to Malaya in a full bottle	62nd	A	—	1090"
	Retested in Malaya	51st	F	795"	—
	Retested in Malaya	93rd	A	975"	—
5	Sample drawn from ship's tank at Liverpool	28th	F	—	980"
	Returned to Malaya in a full bottle	51st	F	879"	—
	Retested	93rd	A	1137"	—

NOTE.—After testing on the 28th day, Sample 4 was divided into three parts; one was returned in a full bottle to Malaya while the other two were kept in the U.K., one in a full and one in a partially-full bottle.

on arrival in the U.K. Samples 4 and 5 were tested immediately on arrival and were then returned by air to Malaya in full bottles for retesting. The initial M.S.T. of each sample and its subsequent history is recorded in Table I.

Testing both in Malaya and the U.K. was carried out on a Dunlop-Klaxon high-speed stirrer⁶. The speed of both stirrers, or more precisely the speed of the center reed which vibrates when the stirrer speed is correctly set at 14,000 r.p.m., was checked with a stroboscope before the commencement of the test series. All test conditions were in accordance with the relevant B.S.I. specification⁶, except that the total solids of the latex was reduced from 62.1 to 58 per cent rather than 55 per cent before testing. M.S.T.'s at 58 per cent may be transformed to 55 per cent by applying a factor of 1.2.

The wide range of M.S.T. figures in Table I cannot possibly be ascribed to any hidden instrumental differences, or differences in testing conditions between Malaya and the U.K., since the highest and lowest figures were both recorded in Malaya. When, however, the results are divided into those in which the latex has stood in a full bottle and those in which it has stood in a

partially-full bottle prior to test, two trends may be distinguished. Whenever the latex stood in a full bottle, the M.S.T. fell; whenever it stood in a partially-full bottle the M.S.T. rose. This is made clear in Figure 1, in which results from Table I are plotted graphically. The fall of M.S.T. during shipment in a ship's tank may, therefore, be ascribed to the exclusion of air from the latex in the tank. A small amount of air is unavoidably sealed into the ship's tank with

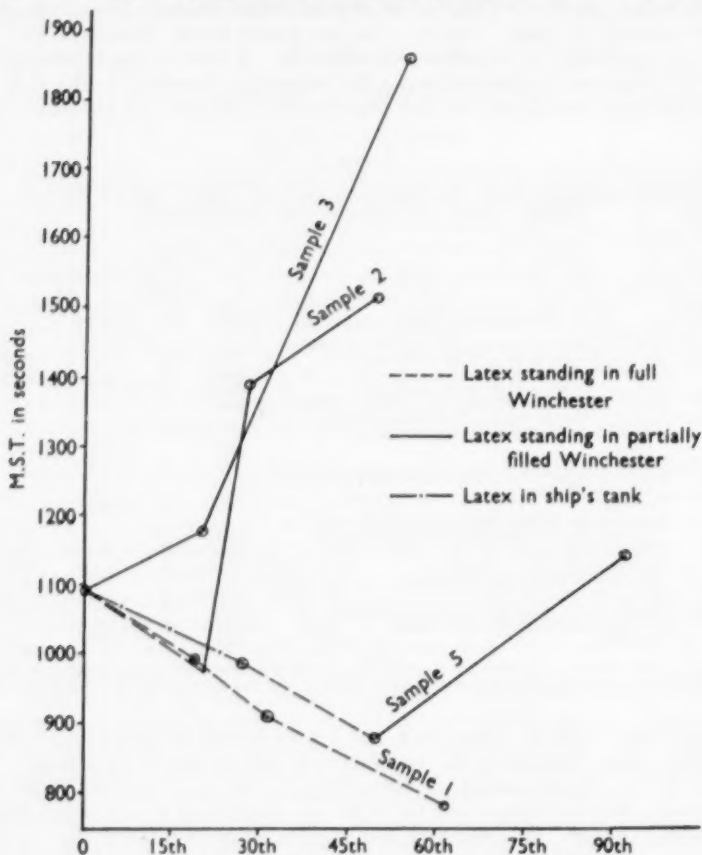


FIG. 1.—M.S.T. of various samples of latex from a single ship's tank of centrifuged concentrate.

the latex, but its volume compared to the total volume of latex is so small that it affects the M.S.T. of the bulk to only a minor extent. Comparison of the M.S.T. figures of the shipments in Table I shows that, on the average, the M.S.T. of a sample taken in Singapore and carried to the U.K. in a full winchester on board the latex tanker is 40 seconds less than that of the bulk on arrival in the U.K. (cf. Samples 4 and 5 in Table I).

McGavack and Bevilacqua¹ were concerned in the earlier part of their work with poorly preserved latex, and it should perhaps be mentioned that the latex

used in Table I was well-preserved, having a volatile fat acid content⁷ of 0.11 at the time of shipment. Starting with a latex already two months old, it has been possible to obtain within a month, M.S.T. values that vary by more than a factor or two, merely by standing one sample of the latex in a partially-full bottle and the other in a full bottle. This does not mean that the M.S.T. test should be abandoned, but rather that all samples for M.S.T. testing should be stored under strictly controlled conditions, which approximate as closely as

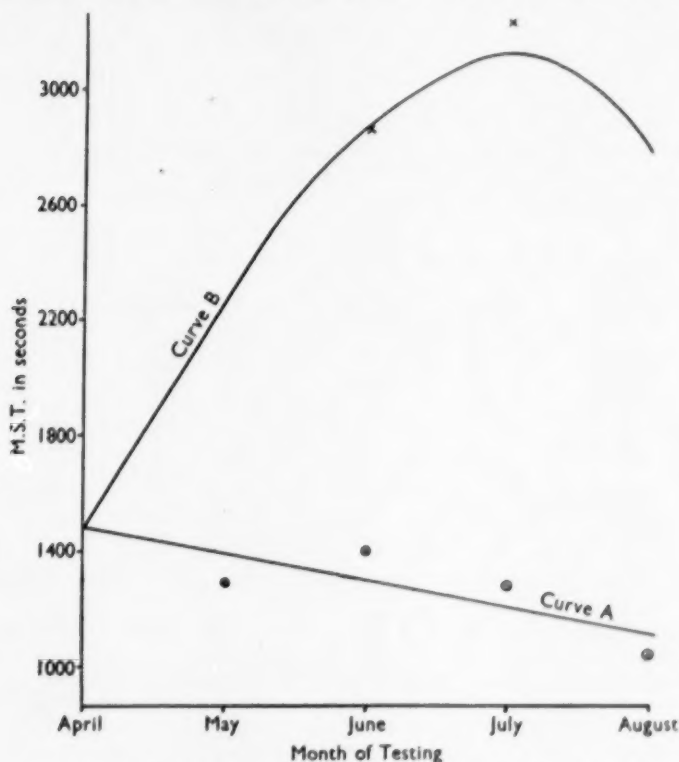


FIG. 2.—M.S.T. of latex standing in a full bottle (Curve A) and in the presence of oxygen (Curve B).

possible to those of the bulk. This usually means that the latex must be kept in a full bottle prior to testing, and that if a series of test figures is required over a period of time, then a separate sealed bottle must be opened on each occasion.

This was the procedure adopted in recording Curve A in Figure 2. In this experiment samples of a 6-week old concentrate were used. Besides the winchester bottles sealed to provide at monthly intervals figures for Curve A, a further sample (Sample B) was taken in which an appreciable air space was left above the latex. Before sealing, oxygen was passed through this air-space (but not, however, through the latex itself) for a period of five minutes. When sealed, the latex was briefly shaken and then let stand undisturbed for one

month. After testing, the same procedure was repeated and the latex was let stand a further month before retesting. From Figure 2, it is seen that in the absence of air (Curve A) the M.S.T. fell 25 per cent in four months; while in the presence of oxygen (Curve B) it rose well over 100 per cent in three. In three months it had apparently reached a maximum, since a fall is recorded during the fourth month. Figures 1 and 2 show conclusively how greatly even small quantities of oxygen affect the M.S.T. of latex.

It must be borne in mind, however, that the magnitude of the effect will vary greatly with slight changes in conditions and particularly with the age of the latex as well as the degree and method of preservation. The pumping of latex from the ship's tank in the consuming country will mix a varying quantity of air with the latex, and this air may prevent any further fall in M.S.T. The clonal make-up of the latex and the time of year at which it has been harvested also is probably of importance. A few figures available on the samples representing the last month of testing in Figure 2 (Samples A and B for short) give some indication of the probable nature of these changes (Table II).

TABLE II

Sample	C	A	B			
Test	Latex tested at commencement of experiment	Standing four months in a full bottle	Increment of A over C	Increment of A over C (%)	Standing four months in presence of oxygen	Increment of B over C (%)
Date of testing	April	August			August	
Ammonia (NH_3 % on latex)	0.61	0.53	-0.08	—	0.52	-0.09
M.S.T. (seconds)	1489	1040	-1440	-30	2620	1140
Sp. conductivity at 30° C ($\text{mbos} \times 10^{-3}$)	—	5.06	—	—	5.51	—
KOH No.	0.72	0.88	—	—	0.97	—
Volatile fat acid content	0.125	0.280	0.155	+124	0.160	0.035
Acid value (g. KOH/100 g.) solids*	—	0.21	—	—	0.20	—
Odor	Fresh	Slightly malodorous	—	—	Fresh	—

* The acid value is the acid value of the ether-soluble portion of the acetone extract of the dried film.

It is well known that small soap additions increase the M.S.T. of latex⁵, and Kidder⁶ has already recorded a marked increase of the acid value of latex in his aging experiments. This increase of acid value is due to the formation in the latex of ammonium soaps similar in nature to ammonium oleate⁶. It is most surprising, therefore, that Sample B has not a higher acid value than Sample A. The increase of M.S.T. in Sample B must be ascribed to some other cause than a higher rate of fat acid formation. Equally surprising is the fact that the volatile fat acid content of Sample A from which air was excluded is markedly higher than that of Sample B where oxygen was present. The increase in V.F.A. for instance, during the test period is more than four times as great in the absence of oxygen. This increase indicates the rapid formation in the latex of ammonium acetate, or more precisely of the ammonium salts of volatile fat acids. The addition of small quantities of ammonium salts decrease rapidly the M.S.T. of latex, and their formation would in itself be more than adequate to explain the fall of M.S.T. recorded in Curve A (Figure 3).

The Rubber Research Institute of Malaya⁷ has recently discussed the survival of bacteria in latex after ammoniation and processing. Anaerobic bacteria are thought to be responsible for the formation of volatile acids in latex and there is, therefore, some likelihood that the changes noted in this

paper, as taking place in the absence of oxygen, are due to anaerobic bacteria. This suggestion is supported by the slightly malodorous nature of Sample A in Table II.

It is planned to carry out further work to study the absorption of oxygen by preserved latex throughout storage and shipment as well as the possible effects that it may have on the final processing characteristics of the latex. In particular, the role of trace metals in affecting oxygen absorption will be considered.

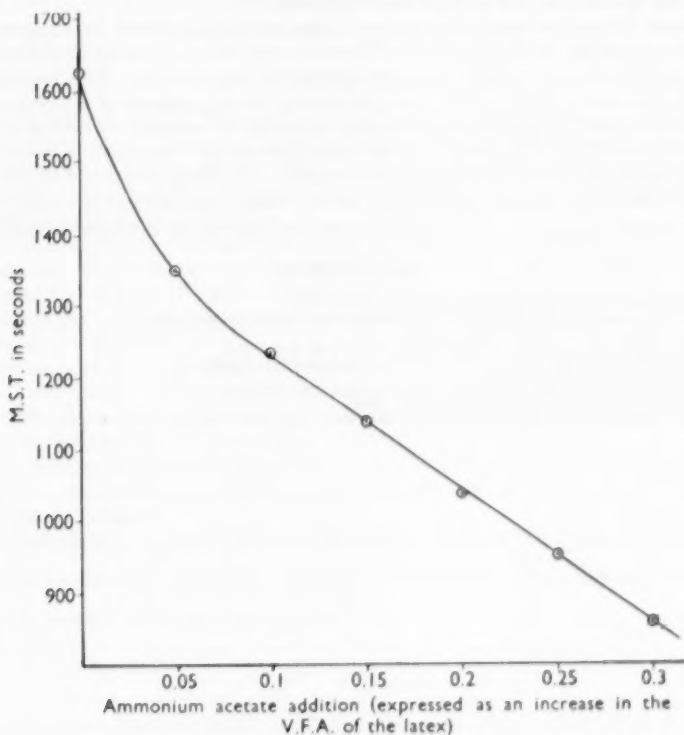


FIG. 3.—Effect of ammonium acetate additions on the M.S.T. of 62% latex.

There is no doubt that a full examination of the underlying causes of the effects described in this paper will give results of wide interest and have a bearing on the formulation of new preservative systems.

ACKNOWLEDGMENTS

The author's thanks are due to many colleagues both in Malaya and in the U.K. for discussions which led to the investigations reported here being undertaken, and to those colleagues in the U.K. responsible for carrying out many of the determinations, particularly those on the exchange samples discussed in the earlier part of the paper. Appreciation is also expressed to Dunlop Malayan Estates Ltd. for permission to publish this paper.

SUMMARY

Working with ammonia-preserved natural-rubber latex, concentrated by centrifuging, the author shows that the slight fall in mechanical stability associated with the shipment of bulk supplies of latex can be explained by the fact that, during shipment, latex does not have access to the oxygen of the air. The mechanical stability of samples taken at the time of shipment increased in value when there was an appreciable air-space in the storage bottle, but fell when the bottle was full and air was excluded.

These differences were accentuated when air was replaced by oxygen and was then possible to find marked differences not only in mechanical stability time but also in the volatile fat acid content of the latexes. The increase of volatile fat acid content of the samples stored in the absence of air was much greater than in the sample stored in the presence of oxygen. The fall of mechanical stability in the absence of air is ascribed to the formation of increasing quantities of salts, such as ammonium acetate. In the presence of oxygen, the rate of formation of salts of this type is very much less, and at the same time other changes take place which lead to a marked increase of mechanical stability.

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COMPARISON OF DIFFERENT VISCOMETERS FOR MEASURING THE VISCOSITY OF LATEX *

(Miss) M. BOUCHER

FRENCH RUBBER INSTITUTE, PARIS, FRANCE

INTRODUCTION

Since latex is a non-Newtonian and thixotropic liquid, certain difficulties are encountered in measuring its viscosity, and the results depend on the apparatus used for the measurements. It seemed, therefore, of interest to compare some of the models now being used and thus to obtain a more definite idea of their possible uses.

To this end we have examined some results obtained with the falling-ball viscometer, which has become the standard in France, the Brookfield viscometer, and the Epprecht-Drage viscometer. Before entering into a description of these types of apparatus, it may be helpful to outline briefly some of the basic concepts of viscosity¹.

Let us consider, in a liquid, two parallel elements of its surface, S , e distant apart, and these two elemental surfaces separated by a liquid. To displace one of the surfaces at a velocity v parallel to the other surface, a definite force F which depends on the nature of the liquid must be exerted.

At the same time, the liquid elements between the two surfaces are displaced parallel to themselves at a continuously varying velocity (from v to 0) in a perpendicular direction.

Consequently, at each point of the liquid between the surfaces there is a velocity gradient, $\frac{dv}{de}$, which is a function of F and S . These different parameters are related in the following way:

$$F = \eta \cdot S \cdot \frac{dv}{de}$$

where η , a characteristic factor of the substance, is called the coefficient of viscosity and is generally measured in poises.

Let us consider the relation: $F = \eta \cdot \frac{dv}{de}$, or better, the function:

$$\frac{dv}{de} = \frac{1}{\eta} \cdot F \quad (1)$$

If the relation is linear, η is constant and is a measure of the angle between the line (I) with the Y-axis (Figure 1). Fluids conforming to this condition are called normal or Newtonian ones.

In most cases, however, and such is the case with latex, the relation (1) is not a linear one.

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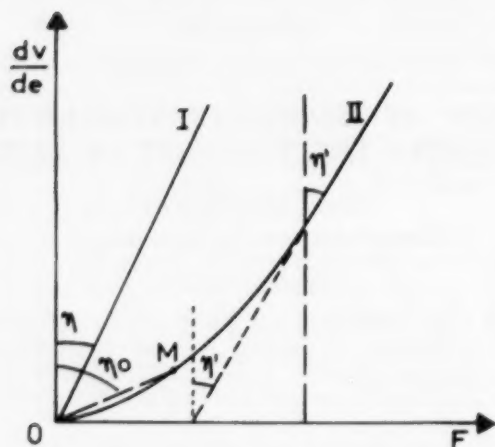


Fig. 1.

In other words, for each value of $\frac{dv}{de}$ (or F) there corresponds a variable value, and the liquid is said to be non-Newtonian. For latex, the curve $\frac{dv}{de} = f(t)$ is shaped approximately like curve (II) in Figure 1, and for each value of F there is a viscosity value expressed by the angular coefficient of straight lines such as OM.

However, with a sufficiently high velocity gradient, the function may be considered as linear and the viscosity coefficient η is then practically constant. This limiting viscosity coefficient is characteristic of such abnormal liquids.

In order that viscosity measurements are comparable in such a case, the conditions must approximate this limiting viscosity. Moreover, since the viscosity is influenced by the velocity gradient, it is necessary to use a method which gives a constant velocity gradient at all points of the liquid and to vary this rate gradient considerably. Only under these conditions is it possible to know when the limiting viscosity is reached. Such conditions are realized in an apparatus with coaxial cylinders based on the Couette method². Several types of this kind are found, but one of the most up-to-date ones is the Drage coaxial cylinder viscometer, described by Epprecht³.

THE DRAGE-EPPRECHT VISCOMETER

A diagram of this apparatus is given in Figure 2. The rotor includes a moving cylinder A with a cone at both ends, rotating at 20, 64, and 200 r.p.m. inside a fixed container B, so that the thin layers of liquid in the container are submitted to a shearing stress.

The starter of the driving motor D is mounted on ball-bearings and stopped in rotation by a torsion wire E. The torsion torque of this wire is equivalent, through the motor, to the torque opposing the rotation of A, and may therefore be measured by the rotation angle at its end. The speed is adjusted through a gear case C.

When A is rotating, the movement is braked down by the viscosity of the

liquid and a balance is established with the torsion wire. The viscosity is calculated from the rotation angle by using the calibration curves supplied with the apparatus. There are 15 curves for the 5 cylinders A coupled to 5 containers B with 3 possible r.p.m.

FALLING-BALL VISCOMETER

While the theory of the coaxial cylinder apparatus is rather simple, the case is different with the Hoppler type ball apparatus, in which a ball slides down

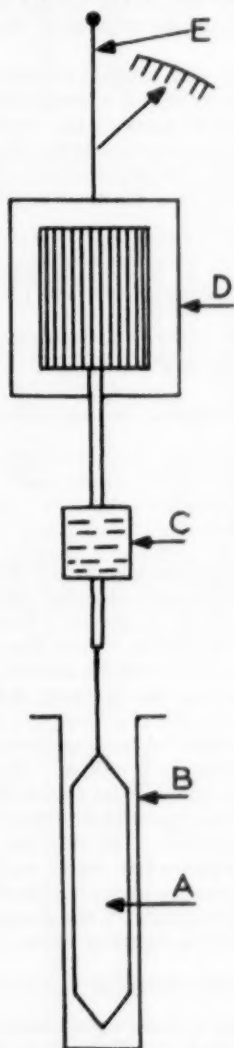


FIG. 2.—Diagram of the Epprecht-Drage viscometer.

inside an inclined tube. Although this type gives but relative values, it is currently used because measurements are rapid and very easy⁴.

It is sufficient to measure the time taken by a steel ball to cover a fixed distance through the liquid in the inclined tube. This time depends on both the viscosity of the liquid and the density differential between the ball and the liquid:

$$\eta = K (d_1 - d_2) t$$

where d_1 is the density of the ball; d_2 the density of the liquid; t the time, and K a constant which depends on the apparatus, especially the respective diameters of the ball and tube.

By calibrating previously with a liquid of known viscosity (measured with an apparatus giving absolute values) it is possible to calculate the coefficient K for a given ball and therefore to measure the viscosity of any liquid.

While no difficulties are encountered with Newtonian liquids, the case is different with abnormal liquids, for which value η depends on the value of t , so that different η values are found for the same liquid with different balls.

TABLE I
COMPARATIVE VISCOSITIES OF NEWTONIAN LIQUIDS MEASURED BY THE
BROOKFIELD, EPPRECHT-DRAGE, AND I.F.C. VISCOMETERS

Reference viscosity	Brookfield				Epprecht-Drage				I.F.C.	
	Rotor no. 1		Rotor no. 2		Rotor A		Rotor B		Ø 11.5	Ø 11.9
	60	30	60	30	64	200	64	200	mm. ball	mm. ball
	r.p.m.	r.p.m.	r.p.m.	r.p.m.	r.p.m.	r.p.m.	r.p.m.	r.p.m.	K =	K =
19 cps	19	18			19	19.5			19.7	19.1
29 cps	28.8	28.8	30	29	29	29.4			29.5	29.2
51 cps	50.5	51	52	51	52	50.5			49.7	
87 cps	86.2	87	86	87.5	86.8	86.5		88	87.5	
120 cps			121	120			121	123	118	
310 cps			320	300			301	306	314	
379 cps			378	372			381	385	374	

However, it was shown by Compagnon and Resplandy⁵ that an apparatus based on this principle could be used when the diameters of the tube and balls were carefully chosen. Choosing one diameter for the tube, they calibrated the unit with liquids of known viscosities. Then they determined the viscosity of numerous latexes and showed that, within certain limits, the values found for viscosity were identical, whatever the diameter of the ball, i.e., the duration of the fall.

The conclusion was that under chosen operating conditions, the figures were fairly independent of the velocity gradient. These results were checked in various laboratories, and the method was standardized⁶.

The apparatus includes essentially a calibrated tube of 12 to 12.3 mm. diameter, placed in a thermostatic box. The time taken by the ball falling in the liquid to cover a distance between two marks on the tube is measured. This time is proportional to the viscosity under standard operating conditions. The coefficient of proportionality depends on the diameters of ball and tube and is determined by calibration with a liquid of known viscosity.

THE BROOKFIELD VISCOMETER

The third type is a rotating cylinder apparatus, but contrary to the Epprecht type described above, the rotating cylinder is moving through a theoretically

TABLE 2
VISCOSITIES OF LATEXES OF DIFFERENT DILUTIONS MEASURED BY THE
I.F.C., EPPRECHT-DRAGE, AND BROOKFIELD VISCOMETERS

I.F.C. Viscometer $K = 1.06$		Epprecht-Drage				Brookfield			
Fall time	Viscosity	Rotor A		Rotor B		Rotor 1		Rotor 2	
		200 r.p.m.	64 r.p.m.	200 r.p.m.	64 r.p.m.	60 r.p.m.	30 r.p.m.	60 r.p.m.	30 r.p.m.
168"/7/10	159			150	222			385	520
105"	99		100					217	310
99"/7/10	94		92	116			202	170	213
81"/6/10	77		76	81			150	131	149
67"/8/10	64	53	60	74		99	121	107	125
50"/8/10	48	41	46	57		72	86	74	87
32"/9/10	31	28	30	36		40	44	45	
21"/7/10	20.5	25	24			27	36		
15"/9/10	15	15	16			17	20		

infinite liquid, since the outer cylinder is replaced by a much larger latex container. The driving motor is linked with the cylinder through a torque-measuring device made of a spiral spring. The rotation is braked by the viscosity of the liquid and a balance is established with the strength of the spring.

The rotation angle of this spring is measured on a calibrated dial, so that the viscosity in centipoises can be determined by a simple coefficient which depends on both the rotation speed and the rotor diameter. Rotors of various diameters are found, and the rotor speed can vary. The diameter and r.p.m. are chosen and combined according to the viscosity of the liquid.

EXPERIMENTAL RESULTS

We have first checked the viscosity of Newtonian liquids with the three types of apparatus: French Rubber Institute (I.F.C.), Epprecht-Drage, and Brookfield. The liquids were oils; their viscosities at different temperatures had been accurately determined by the Institut Francais du Petrole with a viscometer giving absolute values. The results are given in Table 1.

It appears that the values given by the three viscometers do not differ by more than 2 per cent from the absolute values, which is quite satisfactory for industrial devices.

TABLE 3
COMPARATIVE VISCOSITIES OF LATEX MEASURED BY THE FALLING-BALL,
EPPRECHT-DRAGE, AND BROOKFIELD VISCOMETERS

I.F.C. Viscometer		Epprecht-Drage				Brookfield			
Fall time	Viscosity	Rotor A		Rotor B		Rotor 1		Rotor 2	
		200 r.p.m.	64 r.p.m.	200 r.p.m.	64 r.p.m.	60 r.p.m.	30 r.p.m.	60 r.p.m.	30 r.p.m.
6"/7/10	11 cps	9	9			11			
11"/9/10	16	14	15			19	19		
20"/8/10	29	25	28			34	40		
22"/5/10	32	28	30	35		42	48	44	
30"/5/10	40	33	41	43				51	
32"	45	38	44			66	79	66	90
36"/5/10	51		49	61					
44"	63	51	58	72		94	117	104	
50"/5/10	72		68	75				120	140
62"/5/10	80		84	94				183	245
67"	90		90	112			193	162	200
74"	101		99					224	275
	Latex + thickeners								
40"	54	64	77					246	404
164"	210			175	310			580	784

The measurement was then applied to latexes with widely different viscosities obtained either by dilution or thickening.

The results are given in Tables II and III (Figure 4). The figures in Table II are for Gelitex, i.e., a specially thermosensitized latex with a very high viscosity under normal conditions. The values in Table III are for a latex concentrated by centrifugation.

Our measurements were extended up to a viscosity of 200 centipoises, although the figures are not easily interpreted for such high values. Even with the coaxial-cylinder instrument, the torque of the wire is very important when



Fig. 3.—French Rubber Institute (I.F.C.) viscometer.

the viscosity is too high, so that a larger layer of liquid must be used (with a smaller diameter rotor) and conditions are farther from the limiting viscosity. Such defects are much more marked in the Brookfield and French Rubber Institute viscometers.

With these reservations, it appears that when using the Epprecht apparatus, the figures with Rotor B are higher than with Rotor A of a larger diameter. This is in line with the theory that as thin a layer as possible should be used to have a uniform velocity gradient. On the other hand, viscosity values decrease when the rotation speed increases, since values approach progressively towards the limiting viscosity. We may consider that the limiting viscosity is practically attained with this apparatus when the viscosity values do not exceed 100 centipoises, since the values for 64 r.p.m. and 200 r.p.m. are about constant. Naturally, the lower the viscosity, the more nearly alike are the values.

On the contrary, for values over 100 centipoises, the values are markedly different for various rotation speeds (farther from the limiting viscosity).

It is also noted (under 100 centipoises) that results with the French Rubber Institute apparatus approximate fairly well the results with the Epprecht (especially at 64 r.p.m.), i.e., they tend toward (but do not reach) the limiting viscosity.

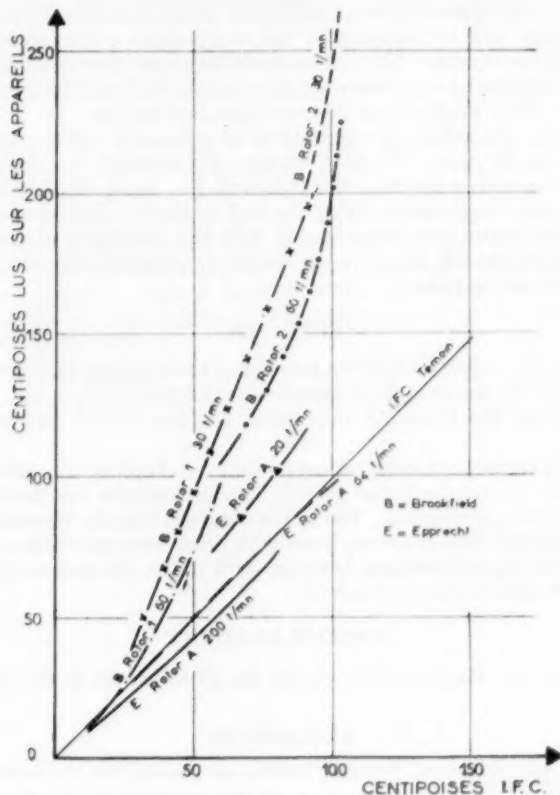


FIG. 4.—Comparison of the Brookfield, Epprecht, and French Rubber Institute viscometers (the last as standard).

Finally, the Brookfield apparatus, even from above 30 centipoises, gives much higher values, particularly when the viscosity is increased. Ideal conditions are, therefore, much less approximated than with the two other types. This is a result of the Brookfield design, where the rotor is moving in an infinite layer of liquid; thixotropy cannot be overcome, and the velocity gradient varies considerably in the various layers from the center to the ends.

CONCLUSIONS

As far as practical results are concerned, a distinction should be made between latex, a raw material which we try to standardize and specify, and industrially processed latex.

In the first case, we try to determine one of the characteristic values of latex by operating as close as possible to the limiting viscosity conditions so as to obtain a value which is independent of the method of measurement.

The most convenient type would, therefore, be the Epprecht-Drage apparatus up to 100 centipoises, a value never exceeded with normal latexes, unless concentrated by evaporation.

However, the Epprecht-Drage apparatus is too expensive for many laboratories and may well be replaced by the much more economical and simple standard ball viscometer. The values are then quite similar to Epprecht values, but care should also be exercised when the velocity is above 100 centipoises, i.e., mostly with either thickened or filler-compounded latexes.

For simply obtaining the viscosity of a motionless latex, the Brookfield apparatus may be used. On the contrary, for assessing the viscosity in the course of processing, when the latex is moved, i.e., when the thixotropic effect disappears, the best choice is either the ball or the coaxial-cylinder type. In any case, the results vary considerably with the conditions of measurement. Such conditions should, therefore, be specified; otherwise the final values can not be considered as valid.

SUMMARY

The viscosity values of different samples of latex diluted to different degrees were measured by means of three viscometers of different types, viz., the Brookfield viscometer, the Epprecht viscometer, and the French Rubber Institute viscometer.

The results obtained are dependent on the type of apparatus, although within certain limits, the Epprecht and French Rubber Institute viscometers give approximately the same results. The values obtained with the Brookfield viscometer are distinctly different from those with other two viscometers.

In spite of these differences, however, each of the viscometers has a field of use, which is indicated and discussed.

ACKNOWLEDGMENT

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COMPARISON OF THE DYNAMIC PROPERTIES OF NATURAL RUBBER AND GR-S

L. J. ZAPAS, S. L. SHUFLE, AND T. W. DEWITT

MELLON INSTITUTE OF INDUSTRIAL RESEARCH, PITTSBURGH, PENNSYLVANIA

A paper by this title was published in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 29, No. 3, pages 725-734, July-September 1956. In this paper, the senior author was spelled PAPAS, whereas it should have been ZAPAS. This unfortunate error is now corrected in this issue of RUBBER CHEMISTRY AND TECHNOLOGY, and future users of this journal will find the name ZAPAS correctly spelled in the annual index and in future cumulative indexes. The indexes will also include the name PAPAS, which will be referred to ZAPAS. This should minimize any possible future confusion arising from the original misspelling of the name.

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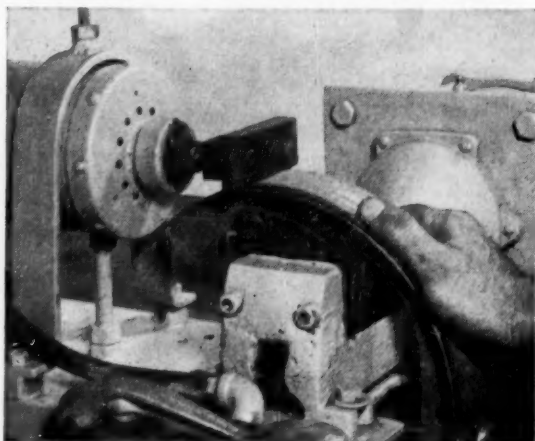
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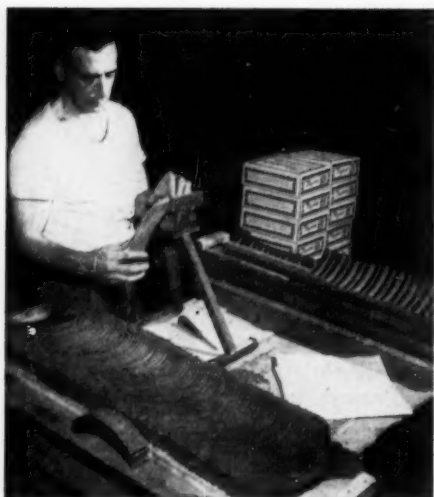
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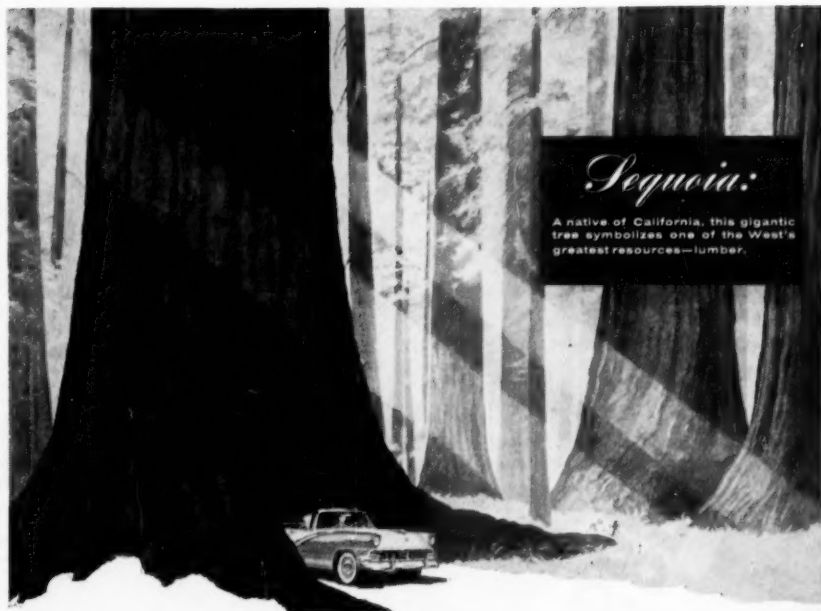
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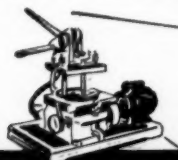
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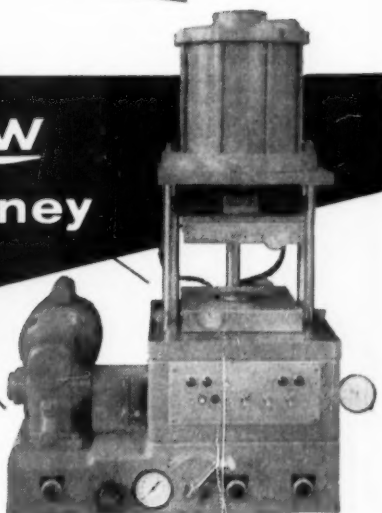
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